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- BASIC DDC.-

G11B9/00

⑪ Publication number:

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⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: 87311397.1

㉓ Int. Cl.4: G11B 9/08 , G11B 9/10

㉒ Date of filing: 23.12.87

㉔ Priority: 24.12.86 JP 309433/86
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(54) Recording device and reproducing device.

(57) A recording device, comprising a probe electrode, a recording medium having electric memory effect and a writing voltage applying means for applying voltage onto the recording medium from said probe electrode, and a reproducing device comprising a probe electrode, a recording medium exhibiting electric memory effect or a recording medium recorded by energy irradiation, a voltage applying means for applying voltage not exceeding the threshold value voltage giving rise to electric memory effect onto the recording medium from said probe electrode and a reading means for reading the change in current quantity passing through said recording medium.



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EUROPEAN SEARCH REPORT

Application Number

EP 87 31 1397

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
X	US-A-4 575 822 (CALVIN F. QUATE) * column 1, lines 55-63; column 2, lines 18-24; column 4, lines 18-19; figures 1,3 *	1,2,17, 25,31- 33	G 11 B 9/08 G 11 B 9/00 G 11 C 11/21
X	GB-A-2 051 456 (NIPPON HOSO KYOKAI et al.) * page 1, lines 53-77; page 2, lines 18-24; figure 1 *	1,7,10, 17,25, 33	
X	EP-A-0 174 860 (XEROX CORP.) * claims 1,2; figure 7; page 9, lines 16-18 *	1,2,17, 25,31- 33	
X,P	EP-A-0 247 219 (IBM CORP.) * column 2, line 48 - column 3, line 18; figure 4 *	1,2,16, 17,25, 33	
A,D	ELECTRONICS LETTERS vol. 20, no. 20, 27th September 1984, pages 838,839; N.J. THOMAS et al.: "GaAs/LB film miss switching device" * complete document *	30	TECHNICAL FIELDS SEARCHED (Int. Cl.3)
A,D	THIN SOLID FILMS vol. 99, 1983, pages 277-281; G.L. LARKINS et al.: "Langmuir-blodgett films as barrier layers in josephson tunnel junctions" * page 280, lines 11-19 *	30	G 11 B 9/00 G 11 B 11/00 G 11 C 11/00
X	EP-A-0 186 813 (BAYER AG) * page 12, lines 12-16; claim 1; figure 1 *	1,2,17, 25	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
BERLIN	02-12-1988	GERARD E.A.S.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
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O : non-written disclosure	L : document cited for other reasons		
	A : member of the same patent family, corresponding		



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EUROPEAN SEARCH REPORT

Page 2

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.3)			
X	EP-A-0 049 076 (HITACHI LTD.) * page 8, line 19 - page 9, line 17; page 13, lines 15-16 * ---	1,7,10, 27-29				
L	PHYSICAL REVIEW LETTERS vol. 49, no. 1; 5th July 1982, pages 57-61; G. BINNING et al.: "Surface studies by scanning tunneling microscopy" * complete document *					
			TECHNICAL FIELDS SEARCHED (Int. Cl.3)			
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search BERLIN</td> <td>Date of completion of the search 02-12-1988</td> <td>Examiner GERARD E.A.S.</td> </tr> </table>				Place of search BERLIN	Date of completion of the search 02-12-1988	Examiner GERARD E.A.S.
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㉕ Recording device and reproducing device.

㉖ A recording device, comprising a probe electrode, a recording medium having electric memory effect and a writing voltage applying means for applying voltage onto the recording medium from said probe electrode, and a reproducing device comprising a probe electrode, a recording medium exhibiting electric memory effect or a recording medium recorded by energy irradiation, a voltage applying means for applying voltage not exceeding the threshold value voltage giving rise to electric memory effect onto the recording medium from said probe electrode and a reading means for reading the change in

0 272 935 A2

Description**Recording Device and Reproducing Device****BACKGROUND OF THE INVENTION****5 Field of the Invention**

This invention relates to a recording device and a reproducing device. More particularly, the present invention relates to a recording device by use of a recording medium having a layer structure of an organic compound between a pair of electrodes one of which is made a probe electrode, and exhibiting memory effect for the switching characteristic of voltage and current, and also to a device for reproducing the information recorded on the recording medium.

10 Related Background Art

In recent years, uses of memory materials form the nucleus of electronics industries such as computers and their related instruments, video discs, digital audio discs, etc. and developments of their materials are also under active progress. The performances demanded for memory materials may differ depending on uses, but may generally include:

- 15 (1) high density and large recording capacity;
- (2) rapid response speed of recording and reproduction;
- 20 (3) small power consumption;
- (4) high productivity and low cost; etc.

Heretofore, semiconductor memories or magnetic memories employing magnetic material or semiconductor as the base material have been predominant, but with the advancement of laser technique, inexpensive and high density recording media with optical memory by use of an organic thin film such as organic dye, photopolymer, etc. are now emerging in the field of art.

25 On the other hand, recently, a scanning type tunnel microscope (hereinafter abbreviated as STM) capable of observing directly the electron structure of the surface atoms of a conductor has been developed [G. Binning et al, *Helvetica Physica*, Cata, 55, 726 (1982)], and it has become possible to measure both single crystalline and amorphous materials with high resolving power of real space image. Besides, it has the advantage that observation can be made at low power without giving damage by current to the medium. Further, it can be actuated in air and applied to various materials, and therefore a broad scope of applications is expected.

30 STM is based on the phenomenon that tunnel current flows when the probe and an electroconductive substance were made to approach to a distance of about 1 nm with a voltage applied therebetween. This current is very sensitive to the distance change between the both, and by scanning the probe so that the tunnel current may be maintained to be constant, the surface structure of the real space can be drawn and at the same time a variety of information about the total electron cloud of the surface atoms can be read. Although analysis by use of STM is limited to electroconductive samples, it is becoming to be introduced to structural analysis of a monomolecular film very thinly formed on the surface of an electroconductive material, and application as the reproduction technique of high density record by utilizing the difference in the state of individual organic molecules may be also considered.

35 On the other hand, in the prior art, the method of forming a latent image by discharging or current supply by use of a needle-like electrode has been known as the electrostatic recording method, and a large number of applications for recording paper, etc. have been made (Japanese Laid-open Patent Publication No. 3435/1974).

40 The film thickness used for this electrostatic recording medium is order of microns, and there has been no report about an example in which the latent image on said medium is electrically read and reproduced.

45 Also, proposal of a molecular electronic device having imparted to one organic molecule the function of a logic element or memory element, etc. has been presented, and studies about the Langmuir-Blodgett film (hereinafter abbreviated as LB film) which may be regarded as one of the construction technique of molecular electronic device have been actively done. An LB film has laminated organic molecules regularly one molecular layer by one molecular layer, and the film thickness can be controlled in a unit of molecular length, whereby uniform and homogeneous ultra-thin film can be formed. As preparation of the device by making full avail of this specific feature, many attempts have been made to use an LB film as the insulating film. For example, there are tunnel junction element with a metal-insulator-metal (MIM) structure [G. L. Larkins et al, *Thin Solid Films*, 99, (1983)], an electroluminescent element with a metal-insulator-semiconductor (MIS) structure [G.G. Robert et al, *Electronics Letters*, 20, 489 (1984)] or a switching element [N.J. Thomas et al, *Electronics Letters*, 20, 838 (1984)]. According to these series of studies, the element characteristics have been investigated, but the there still remain unsolved problems that reproducibility and stability are lacking, such as variance or change with lapse of time in characteristics in respective elements, etc.

50 In the prior art, the above investigations have been made primarily about LB films of fatty acid which can be handled with relative ease. However, from organic materials which has been deemed to be inferior in heat resistance and mechanical strength, there are being developed heat-resistant and mechanically stronger organic materials one after another. We have studied intensively in order to prepare a MIM element excellent in

reproducibility and stability by using an LB film by use of these materials as the insulator, and consequently could successfully prepare a thin and uniform dy insulating film not found in the prior art. Also, as a consequence, a MIM element capable of exhibiting the switching phenomenon having an entirely novel memory function has been discovered.

5

SUMMARY OF THE INVENTION

More specifically, an object of the present invention is to provide a recording device and a reproducing device by use of a novel high density recording medium having memory characteristic for switching characteristics of voltage and current.

The present invention has specific features in a recording device, comprising a probe electrode, a recording medium exhibiting electric memory effect and a writing voltage applying means for applying voltage onto the recording medium from said probe electrode, and in a reproducing device comprising a probe electrode, a recording medium exhibiting electric memory effect of a recording medium recorded by energy irradiation, a voltage applying means for applying voltage not exceeding the threshold value voltage giving rise to electric memory effect onto the recording medium from said probe electrode and a reading means for reading the change in current quantity passing through said recording medium.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates diagrammatically the current passage recording and reproducing device of the present invention.

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Fig. 2 illustrates the characteristic curve of the current passed when 1 V is applied on the probe electrode when the distance between the probe electrode and the sample (recording layer) is varied.

Fig. 3 illustrates the pulse voltage waveform for recording.

Fig. 4 is a schematic illustration of MIM device.

Figs. 5 and 6 are characteristic graphs showing electrical characteristics obtained in the device shown in Fig. 4.

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Fig. 7 is a schematic illustration of the device for forming built-up film.

Figs. 8A and 8B are schematic illustrations of a monomolecular film.

Figs. 9A to 9Cf are schematic illustrations of a built-up film.

Fig. 10A illustrates diagrammatically the current passage recording and reproducing device of the present invention.

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Fig. 10B is a perspective view of a substrate on which a plural number of probes were provided, and Fig. 10C is a side view thereof.

Fig. 10D illustrates diagrammatically another current passage recording and reproducing device of the present invention.

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Fig. 10E is a perspective view of a substrate on which a plural number of probes are provided, and Fig. 10F is a side view thereof.

Figs. 11A to 11C illustrate schematically the track and the recorded state of data in the recording medium.

Fig. 12A is a schematic illustration of the recording pattern used in the present invention, and

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Fig. 12B is an enlarged view of the line pattern recorded within each lattice.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The recording medium of the present invention, by employing an organic built-up film with molecules having a group having π -electron level and a group having only σ -electron level in combination laminated on an electrode, can exhibit a non-linear current-voltage characteristic different from the prior art by applying current by use of a probe electrode vertical to the film surface.

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Since most of organic materials generally exhibit insulating or semi-insulating properties, a remarkable diversity of applicable organic materials having a group having π -electron level are included in the present invention.

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As the structure of the dye having π -electron system suitable for the present invention, there may be included, for example, dyes having porphyrine skeleton such as phthalocyanine, tetraphenylporphyrine, etc.; azulene type dyes having squarilium group and croconic methine group as the bonding chain and cyanine-like dyes having two or more nitrogen-containing heterocyclic rings such as quinoline, benzothiazole, benzoxazole, etc. bonded through squarilium group and croconic methine group; or cyanine dyes, condensed polycyclic aromatic compounds such as anthracene and pyrene, and chain compounds obtained by polymerization of aromatic ring and heterocyclic compounds; and polymers of diacetylene group; further derivatives of tetraquinodimethane or tetrathiafluvalene and analogues thereof and charge transfer complexes thereof; and further metal complex compounds such as ferrocene, tris-bipyridine ruthenium complexes, etc.

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Concerning formation of an organic recording medium, although the vapor deposition method or the cluster ion beam method may be applicable, an LB method is extremely suitable among the known techniques because of controllability, easiness and reproducibility.

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According to the LB method, a monomolecular film of an organic compound having a hydrophobic site and a hydrophilic site in one molecule or a built-up film thereof can be formed easily on a substrate, which has a thickness on the molecular order and a uniform and homogeneous organic ultra-thin film can be supplied

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stably over a large area.

The LB method is a method in which a monomolecular film or its built-up film is prepared by utilizing the phenomenon that, in a molecule with a structure having a hydrophilic site and a hydrophobic site in a molecule, when the balance of the both (amphiphilic balance) is brought to a proper value, the molecule will form a layer of monomolecule on the water surface with the hydrophobic group directed downward.

Examples of the group constituting the hydrophobic site may include various hydrophobic groups generally known widely such as saturated and unsaturated hydrocarbon groups, condensed polycyclic aromatic groups and chain polycyclic phenyl groups, etc. These may constitute the hydrophobic moiety each individually or as a combination of a plurality thereof. On the other hand, most representative as the constituent of the hydrophilic moiety are, for example, hydrophilic groups such as carboxyl group, ester group, acid amide group, imide group, hydroxyl group, further amino groups (primary, secondary, tertiary, and quaternary), etc. These also constitute the hydrophilic moiety of the above molecule each individually or as a combination of a plurality thereof.

A dye molecule having these hydrophobic group and hydrophilic group in a well-balanced state and having π -electron system having an appropriate size can form a monomolecular film on the water surface, and it can be an extremely suitable material for the present invention.

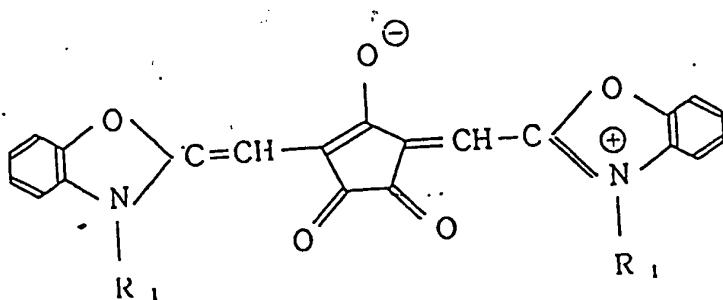
Specific examples may include the molecules as shown below.

[I] Croconic methine dyes:

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1)

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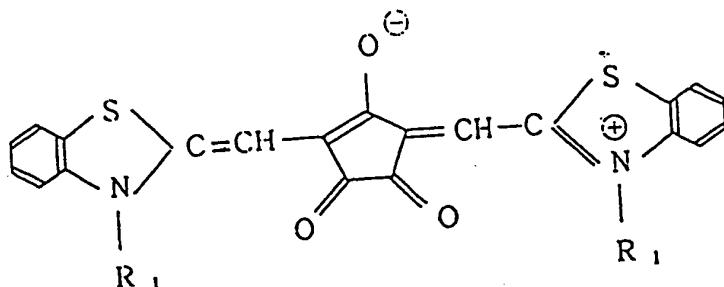


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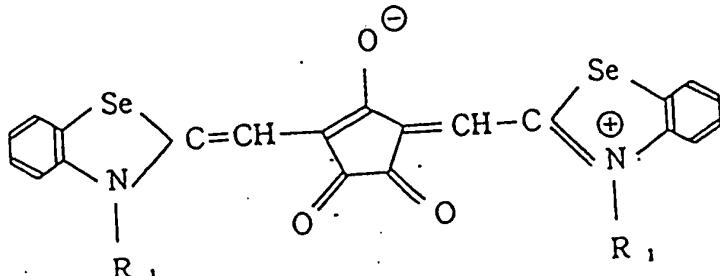


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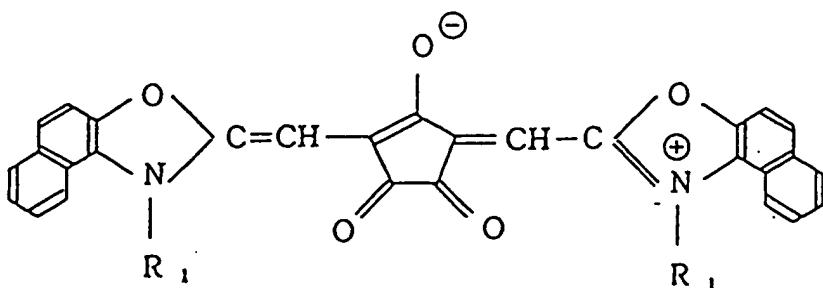
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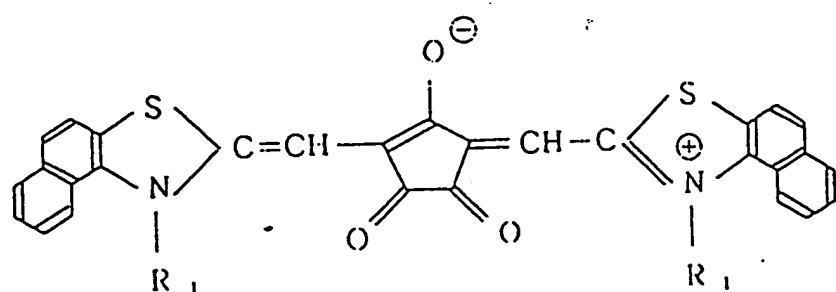
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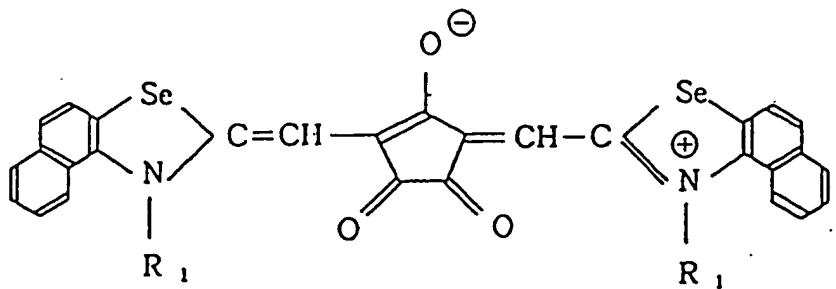
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6)



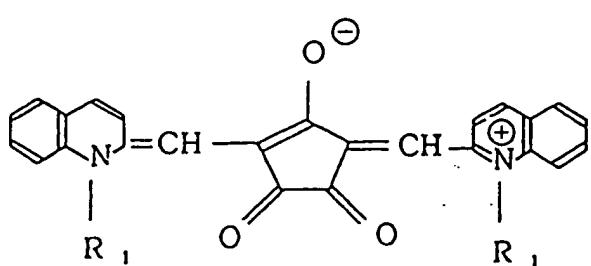
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[I] Croconic methine dyes:

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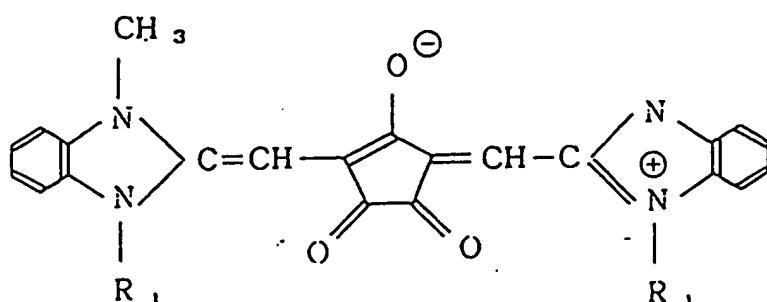
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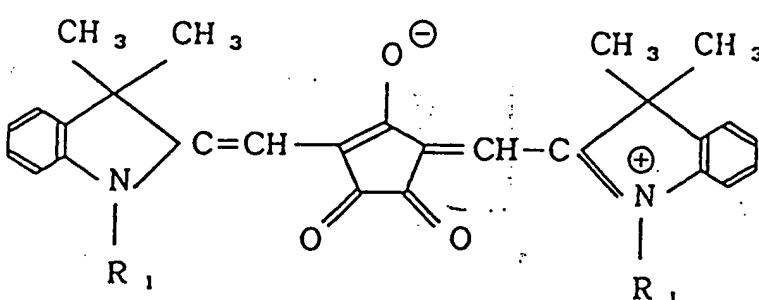
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9)

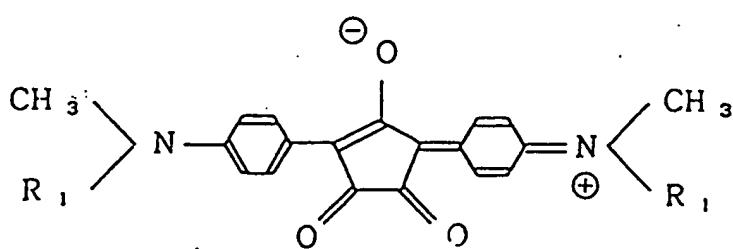


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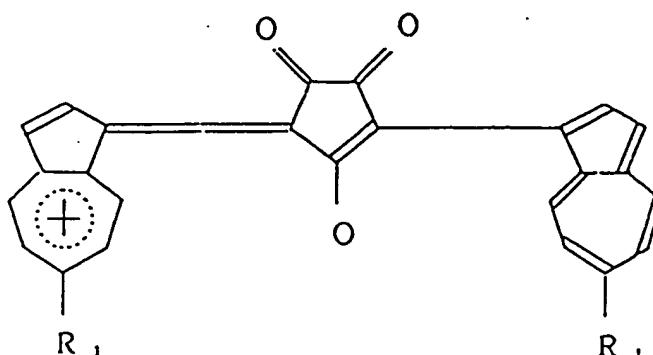
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11)



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wherein R₁ corresponds to the group having π -electron level as mentioned above, and may be preferably a long chain alkyl group introduced with the carbon number n being $5 \leq n \leq 30$ for making easier formation of

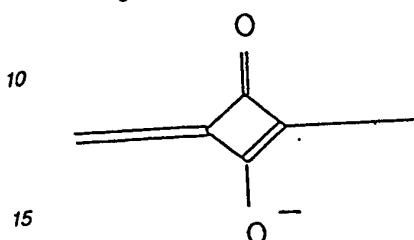
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the monomolecular film on the water surface. The compounds mentioned above as specific examples show only the basic structures, and various derivatives of these compounds are also suitable in the present invention, as a matter of course.

5 [II] Squarilium dyes:

Compounds mentioned in [I] in which the croconic methine groups are replaced with the squarilium group having the following structure:



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[III] Porphyrine type dye compounds:

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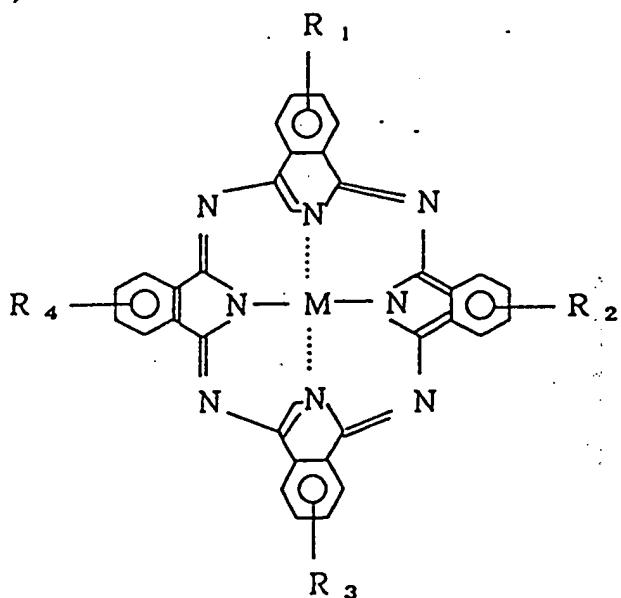
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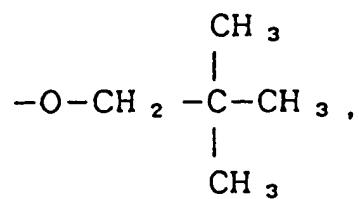
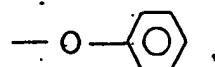
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[III] Porphyrine type dye compounds:

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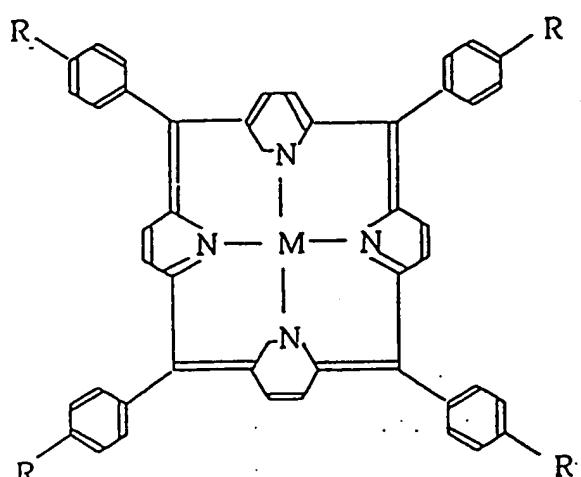
R₁, R₂, R₃, R₄ = II,



M = H₂, Cu, Ni, Al-Cl and

rear earth metal ion

2)



R = OCH(COOH)C_nH_{2n+1}

5 ≤ n ≤ 25

M = H₂, Cu, Ni, Zn, Al-C

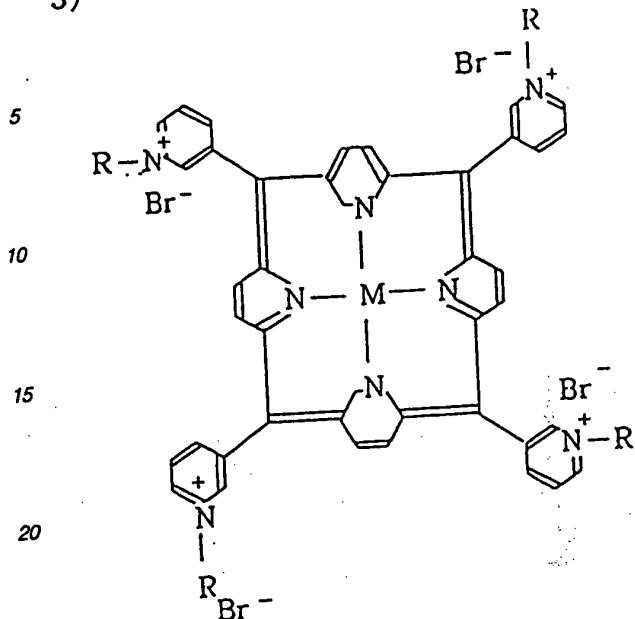
and rear earth metal ion

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3)



$$R = C_2H_{2n+1} \quad 5 \leq n \leq 25$$

$M \equiv H_2, Cu, Ni, Zn, Al-Cl$

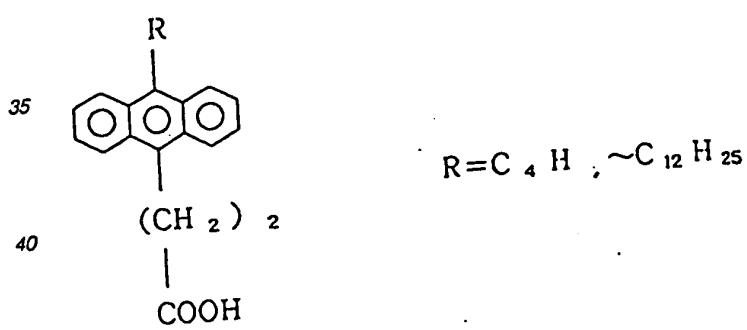
and rare earth metal ion

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R is introduced for making easier formation of the monomolecular film, and is not limited to the substituents mentioned here. On the other hand, $R_1 - R_4$ correspond to the group having σ -electron level as mentioned above.

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[IV] Condensed polycyclic aromatic compounds:



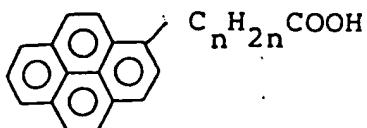
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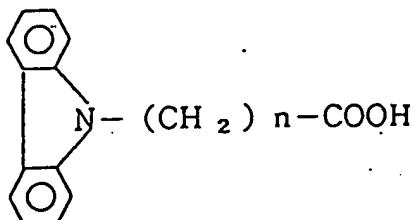


$\sigma \leq N \leq 20$

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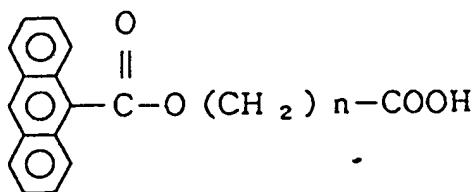
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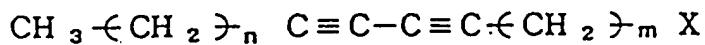
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[V] Diacetylene compounds:



$0 \leq n, m \leq 20$

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(with proviso $n + m > 10$)

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X is a hydrophilic group, and generally -COOH is used, but -OH, -CONH₂, etc. can be also used.

[VI] Others:

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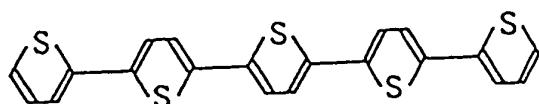
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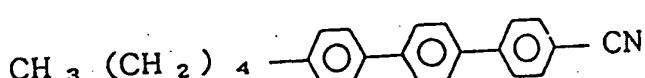
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Quinquethienyl

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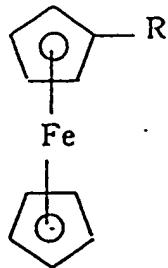
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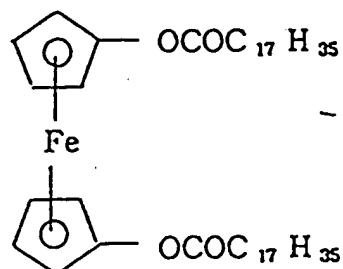
$$R = CONHC_{18}H_{37},$$

$$OCOC_{17}H_{35}$$

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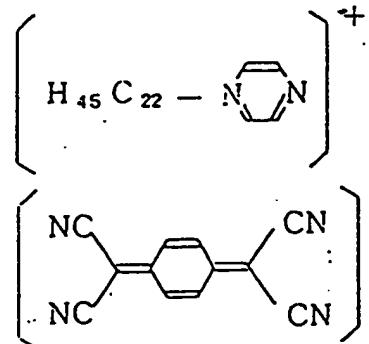
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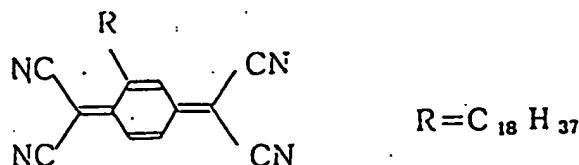


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6)



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Dye materials suitable for the LB method other than those mentioned above are of course suitable for the present invention. For example, biological materials of which study is becoming popular (e.g. bacteriorhodopsin).

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sin or cytochrome c) or synthetic polypeptides (PBLG, etc.) and other may be also applicable.

Such amphiphilic molecule forms a monomolecular film with the hydrophilic group directed downward. The monomolecular layer on the water surface has the characteristics of the two-dimensional system. When the molecules are scattered sparsely, the following formula of the two-dimensional ideal gas is valid between the area per one molecule A and the surface pressure :

5 $\pi A = kT$,
thus becoming "gas film". Here, k is the Boltzmann's constant and T is an absolute temperature. When A is made sufficiently small, intermolecular interactions are strengthened, whereby the molecules become "condensed film (or solid film)" or a two-dimensional solid. The condensed film can be transferred, one layer by one layer, onto the surface of any desired body having various materials and shapes such as glass or resin.

10 By use of this method, a monomolecular film or built-up films thereof can be prepared, and used as the recording layer.

As a specific preparation method, the following method may be employed.

15 A desired organic compound is dissolved in a solvent such as chloroform, benzene, acetonitrile, etc. Next, such solution is spread on an aqueous phase 81 by means of an appropriate device as shown in Fig. 7 in the accompanying drawings to form the organic compound in shape of a film.

Subsequently, a partitioning plate (or a float) 83 is provided to prevent too broad expansion of the spreading layer 82 through free diffusion on the aqueous phase 81, whereby the spreading area of the spreading film 82 is restricted to control the gathered state of the film substance and obtain a surface pressure π in proportion to the gathered state. By moving this partitioning plate 83, the gathered state of the film substance can be controlled by reducing the spreading area, whereby the surface pressure can be gradually elevated to be set at a surface pressure suitable for preparation of the film. With the surface pressure kept constant, by moving vertically a clean substrate 84 gently, a monomolecular film of an organic compound is transferred onto the substrate 84. Such monomolecular film 91 is a film having molecules orderly arranged as shown in Fig. 8A or 8B.

25 The monomolecular film 91 can be thus produced, and a built-up film with desired built-up number can be formed by repeating the above operation. For transfer of the monomolecular film 91 onto the substrate 84, other than the above vertical dipping method, such methods as the horizontal lifting method, the rotating cylinder method, etc., may be employed. The horizontal lifting method is a method in which transfer is effected with the substrate being contacted horizontally on the water surface, and the rotating cylinder method is a method in which the monomolecular layer is transferred onto the substrate surface by rotating a cylindrical substrate on the water surface.

In the vertical dipping method as described above, when a substrate having a hydrophilic surface is withdrawn in the direction transversing the water surface, a monomolecular film 91 of the organic compound with the hydrophilic sites 92 of the organic compound directed toward the substrate 84 side is formed on the substrate 84 (Fig. 8B). When the substrate 84 is moved vertically, monomolecular films 91 are laminated one layer by one layer in the respective steps to form a built-up film 101. Since the direction of the film forming molecules in the withdrawing step becomes opposite to that of the dipping step, there is formed a Y type film according to this method in which the hydrophobic sites 93a and 93b of the organic compound are faced to each other between the respective layers (Fig. 9A). In contrast, in the horizontal lifting method, the monomolecular film 91 is formed on the substrate 84 with the hydrophobic site 93 of the organic compound faced toward the substrate 84 side (Fig. 8A). According to this method, even when the monomolecular film 91 may be built up, there is no change in direction of the film forming molecules, but there is formed an X type film in which the hydrophobic sites 93a and 93b are faced toward the substrate side in all of the layers (Fig. 9B). On the contrary, a built-up film 101 in which the hydrophilic sites 92a and 92b are faced toward the substrate 84 side is called a Z type film (Fig. 9C).

45 The method for transferring the monomolecular film 91 onto a substrate 84 is not limited to the above methods, but it is also possible to employ a method in which a substrate is extruded into an aqueous phase from a roll, when employing a large area substrate. The direction of the hydrophilic groups and the hydrophobic groups toward the substrate as described above are given as a general rule, and it can also be modified by the surface treatment of the substrate, etc.

50 As described above, a potential barrier layer comprising the monomolecular film 91 of an organic compound or its built-up film is formed on the substrate 84.

In the present invention, the substrate 84 for supporting the thin film comprising a lamination of the inorganic material and organic material may be any of metal, glass, ceramics, plastic materials, etc., and further a biological material with remarkably lower heat resistance can also be used.

55 The substrate 84 as described above may be in any desired shape, preferably in a flat plate, which is not limitative of the present invention at all. This is because the above film forming method has such advantage that the film can be formed exactly in accordance with the shape of the substrate surface independently of the shape of the substrate surface.

60 In another specific example of the present invention, it is possible to utilize the phenomenon that tunnel current flows when the probe of a metal and an electroconductive substance are brought close to each other to a distance of about 1 nm with application of a voltage therebetween. This tunnel current depends on the work function on the surface, and therefore information regarding various surface electron states can be read.

65 The method by use of tunnel current has a number of advantages such that it requires no vacuum condition,

is applicable to both single crystalline and amorphous materials, has high resolving power, and yet reproduction at low power is possible without giving damage by the current.

Further, since tunnel current is of a magnitude on the order of about nA, the recording medium may be one having a conductivity of 10^{-10} (ohm.cm) $^{-1}$ or higher, preferably 10^{-6} (ohm.cm) $^{-1}$ or higher.

As the recording medium to be used in the present invention, materials exhibiting the memory switching phenomenon in current-voltage characteristic can be utilized. For example, there may be included (1) amorphous semiconductors such as oxide glass, borate glass or chalcogenide glass containing Se, Te, as compounded with the element of the group III, IV, V or VI of the periodic table, etc. They are intrinsic semiconductors having an optical band gap Eg of 0.6 to 1.4 eV or an electrical activation energy ΔE of approximately 0.7 to 1.6 eV. Specific examples of chalcogenide glass may include A-Se-Te type, Ge-As-Se type, Si-Ge-As-Te type, for example, Si₁₆Ge₁₄As₅Te₆₅ (the subscripts show atomic%), or Ge-Te-X type, Si-Te-X type (X=represents small amount of group V, and VI elements), for example Ge₁₅Te₈₁Sb₂S₂.

Further, a chalcogenide glass of Ge-Sb-Se type may also be used.

In the amorphous semiconductor layer comprising the above compound deposited on the electrode, by applying a voltage in the direction vertical to the film surface by use of a probe electrode, the electric memory effect of the medium can be exhibited.

As the method for depositing such material, the object of the present invention can be sufficiently accomplished according to the thin-film-forming technique known in the art. For example, suitable film-forming methods may include the vacuum vapor deposition method, the cluster ion beam method, etc. Generally speaking, the electric memory effect of such material is observed at a film thickness of several μm or less, and concerning recording resolving power as the recording medium, the thickness may be preferably thinner. However, with respect to uniformity and recording characteristic, a film thickness is preferably 100 Å to 1 μm more preferably a thickness of 1000 Å or less.

Further, there may be included (2) organic semiconductor layers, having deposited a salt of an electron accepting compound such as tetraquinodimethane (TCNQ), TCNQ derivatives, for example, tetrafluorotetra-cyanoquinodimethane (TCNQF₄), tetracyanoethylene (TCNE) and tetracyanonaphthoquinodimethane (TNAP), etc. with a metal having relatively lower reduction potential such as copper or silver on the electrode.

As the method for forming such organic semiconductor layer, there may be employed the method in which the above electron accepting compound is vacuum vapor deposited on the electrode of copper or silver.

The electric memory effect of such organic semiconductor is observed at a film thickness of several ten μm or less, but a film thickness of 100 Å to 1 μm is preferred with respect to film forming property and uniformity.

Further, there may be employed (3) recording medium using amorphous silicon as the material. For example, it is a recording medium having a layer constitution of metal/a-Si (p^+ layer/n layer/i layer) or metal/a-Si (n^+ layer/p layer/i layer), and the respective layers of a-Si can be deposited satisfactorily according to the methods known in the art. In the present invention, the glow discharge method (GD) may be preferably employed. The film thickness of a-Si may be preferably 2000 Å to 8000 Å for the n layer, about 1000 Å for the p^+ layer, with the total film thickness being preferably about 0.5 μm to 1 μm .

On the other hand, the electrode material to be used in the present invention may be one having high conductivity, including a large number of materials, typically metals such as Au, Pt, Ag, Pd, Al, In, Sn, Pb, W, etc. and alloys of these, further graphite or silicide, and further electroconductive oxides such as ITO, and application of these materials for the present invention may be contemplated. The method for forming electrode by use of such material may be sufficiently the known thin film forming technique. However, as the electrode material to be formed directly on the substrate, it is preferable to use an electroconductive material of which the surface will not form an insulating oxide film during formation of an LB film, for example a noble metal or an oxide conductor such as ITO.

The metal electrode of the recording medium is required if the recording layer in the present invention is insulating, but no such metal electrode is required if said recording layer exhibits semiconductive properties of $\text{M}\Omega$ or less. Thus, the recording layer itself can be used as the counter-electrode of the probe electrode.

Also, the tip of the probe electrode is required to be pointed so far as possible in order to enhance resolving power of recording/reproduction/erasing. In the present invention, a platinum with a thickness of 1 mm in diameter with a tip mechanically grounded to a cone of 90°, which is subjected to evaporation of the surface atoms by applying an electrical field in ultra-high vacuum, is employed, but the shape of the probe and the treating method are not limited thereto.

By use of the materials and the method as described above, a device with MIM structure as shown in Fig. 4 was prepared, whereby a memory switching device exhibiting the current-voltage characteristics as shown in Fig. 5 and Fig. 6 was obtained, and the two states (ON state and OFF state) were already found to have respective memory characteristics. These memory switching characteristics appear at the layer thickness of several Å to several 1000 Å, but the recording medium used with the probe electrode of the present invention should preferably have a layer thickness in the range of several Å to 500 Å, most preferably a layer thickness of 10 Å to 200 Å.

In Fig. 4, 84 represents a substrate, 41 an Au electrode, 42 an Al electrode and 43 a built-up monomolecular film as described above.

Fig. 1 is a block constituting diagram showing the recording device of the present invention. In Fig. 1, 105 is a probe current amplifier, 106 a servo circuit for controlling the fine mechanism 107 by use of a piezoelectric element so that the probe current may become constant. 108 is a power source for applying a pulse voltage for

recording/erasing between the probe electrode 102 and the electrode 103.

When a pulse voltage is applied, the probe current will be abruptly changed and therefore the servo circuit 106 controls the HOLD circuit to be set ON so that the output voltage may be kept constant during that period.

109 is an XY scanning driving circuit for movement control of the probe electrode in the XY direction. 110 and 111 are used for coarse control of the distance between the probe electrode 102 and the recording medium 1 so that a probe current of about 10^{-9} A may be obtained. These respective instruments are under central control by means of a microcomputer 112. Also, 113 has a display instrument.

The mechanical performances in the movement control by use of a piezoelectric element are shown below.

Fine control range in Z direction: 0.1 nm - 1 μm

10 Coarse control range in Z direction: 10 nm - 10 mm

Scanning range in XY direction: 0.1 nm - 1 μm

Measurement, control tolerable error: < 0.1 nm.

Fig. 10A is a block constituting diagram showing another recording device of the present invention. In Fig. 10A, 1005 is a probe current amplifier, and 1006 is a servo circuit for controlling the fine mechanism 1007 by use of a piezoelectric element so that the probe current may become constant. 1008 is a power source for applying a pulse voltage for recording/erasing between the probe electrodes 1002a, b, c and the electrode 1003.

When a pulse voltage is applied, the probe current will be abruptly changed, and therefore the servo circuit controls the HOLD circuit to be set ON so that the output voltage may be kept constant during that period.

20 1009 is an XY scanning driving circuit for movement control of the probe electrodes 1001a, b, c in the XY direction. 1010 and 1011 are used for coarse control of the distance between the probe electrodes 1002a, b, c and the recording medium 1 so that a probe current of about 10^{-9} A may be previously obtained. These respective instruments are all under central control by means of a microcomputer 1012. 1013 represents a display instrument, and 1015 a wiring.

25 Also, the mechanical performances in the movement control by use of a piezoelectric element are shown below.

Fine control range in Z direction: 0.1 nm - 1 μm

Coarse control range in Z direction: 10 nm - 10 mm

Scanning range in XY direction: 0.1 nm - 1 μm

30 Measurement, control tolerable error: < 0.1 nm.

Fig. 10D is another preferable example of the present invention, showing a block diagram of the device having a large number of probe electrodes 1002 provided. Fig. 10E showing a perspective view of an embodiment in which a number of probe electrodes 1002 are provided on the SiO₂ substrate and Fig. 10F showing a side view thereof.

35 The probe electrodes shown in Figs. 10D - 10E can be prepared in a large number by implanting silicon onto the SiO₂ plate by focus-ion beam and permitting tungsten to grow selectively on the silicon. In the device shown in Fig. 10D, in place of the servo circuit 1006 used in the device shown in Fig. 10A, an A/D transducer 1016 for converting analog signals obtained to digital signals can be used.

In another preferable example of the present invention, a high density record written by use of an energy beam such as a particle beam (an electron beam or an ion beam) or a higher energy electromagnetic wave ray such as an X-ray, etc. and visible light, an UV-ray or a laser beam, etc. can be electrically reproduced by use of a probe electrode. As a reproducing device, the device shown in Fig. 1 and Fig. 10 can be used. In this case, the recording medium 1 to be used is constituted of a substrate electrode 103 and a recording layer 101 formed thereon.

45 As the recording layer 101 mentioned above, an inorganic or organic semiconductive substance can be used.

For example, inorganic semiconductors may include semiconductive substances containing the element selected from the group IVB of the long period type periodic table (C, Si, Ge), semiconductive substances containing the element selected from the group IIIB (Ga) and the element selected from the group VB (As, P) or semiconductive substances containing the element selected from the group IIB (Zn, Cd) and the element selected from the group VIB (O, S, Se). Specifically, there may be employed a large number of materials, including typically semiconductors such as Si (single crystalline, polysilicon, amorphous), Ge, GaAs, GaP, InAs, InP or CdS, CdSe, ZnO, ZnS, etc. On the other hand, organic semiconductors may include a large number of organic semiconductors, for example, aromatic polycyclic compounds such as phthalocyanine and derivatives thereof, pyren, perylene, etc. and derivatives thereof; polymeric compounds having conjugated π bond such as polyacetylene, polydiacetylene derivatives, etc.; further electrolytic polymerized films such as of pyrrole, thiophene, etc.; or polyvinyl carbazole, tetraquinodimethane, docosylyridinium, tetraquinodimethane charge transfer complexes, etc.

These semiconductor substances can be formed in conventional manner into thin films. For example, for film formation of an inorganic semiconductor, there can be employed the vacuum vapor deposition method, the sputtering method, the glow discharge method, etc., while for film formation of an organic semiconductor, the vacuum vapor deposition method such as the cluster ion beam method or the electrolytic polymerization method may be available. Also, film formation can be effected by coating of a coating liquid having a semiconductive substance dispersed in an appropriate resin (e.g. polystyrene, polyacrylonitrile, polycarbonate, polyester, etc. according to a conventional method (roll coating, dip coating, etc.).

Also, in another specific example of the present invention, during formation of the recording layer 101, a Langmuir-Blodgett method (an LB method) proposed by Langmuir et al as described above is applicable.

As the general structure of molecule to be used in the present invention, the molecules as shown below may be included.

(1) Molecules with the site bearing desired function, namely the functional moiety (e.g. π electron system) having at the same time strong hydrophilic property (or strong hydrophobic property) in combination, for example, copper phthalocyanine, pyrene, triphenylmethane, etc., or molecules with such functional moiety exhibiting polymerizability, for example, diacetylene derivatives, polyimide, etc. 5

(2) Molecules with the functional moiety having not particularly hydrophilic property or hydrophobic property and having hydrophilic sites and hydrophobic sites formed within the molecule by introducing hydrophilic groups, and hydrophobic groups as described above, including, for example: 10

a) those having functional moieties arranged on the side of hydrophilic sites, for example, long chain alkyl-substituted melanocyanine dyes having photo-conductivity, etc.:

b) those having functional moieties arranged on the side of hydrophobic sites, for example, pyrene having long chain alkylcarboxylic acid bonded thereto;

c) those having functional moieties arranged around the center, namely in the middle of the hydrophobic sites and the hydrophilic sites, for example, anthracene derivatives, diazo dyes, etc.

d) those having no functional moiety, but constituting of only hydrophobic sites and hydrophilic sites, for example, stearic acid, arachidic acid, etc. substituted with long chain saturated fatty acid. 15

Other materials suitable for the LB method than those mentioned above are of course suitable for the present invention. For example, biological materials of which studies have been comprehensively made in recent years (e.g. polypeptides such as bacteriorhodopsin or cytochrome c) or synthetic polypeptides (PBLG, etc.) may be also applicable. 20

A potential barrier layer comprising a monomolecular film of such organic compound or its built-up film is formed on the substrate. 25

In the present invention, the substrate for supporting the thin film comprising a laminate of inorganic and organic materials as described above may be any of metal, glass, ceramics, plastic materials, etc., and further a biological material with remarkably lower heat resistance can be also used.

The substrate as mentioned above may have any desired shape, preferably a flat plate shape, but the shape is not limited to a flat plate at all. Thus, in the above film forming method, irrespectively of whether the substrate may have any surface shape, there is the advantage that the film can be formed exactly the same as its shape. 30

The recording layer 101 can be recorded with various energy beams as described below, and the recorded image can be reproduced by means of the reproducing means as described above. In the following, specific examples of the recording method are shown.

1) A method in which a high energy particle beam such as electron beam, ion beam is irradiated on the LB film as described above. By irradiation of a high energy particle beam onto an LB film, there occurs physical change in the film structure of the LB film itself, whereby the change in the film thickness of the LB film is caused to occur. 35

2) A method in which an ion beam, visible light or a UV-ray is irradiated onto the semiconductor thin film, whereby the change in electroconductivity is caused to occur at the irradiated portion.

3) A method in which electron beam is irradiated onto a thin film of a metal phthalocyanine (copper phthalocyanine, nickel phthalocyanine, lead phthalocyanine, etc.), thereby causing the oxidation-reduction reaction of the metal phthalocyanine at the irradiated portion to occur, to cause change in the film structure. 40

4) A method in which change in electron state accompanied with polymerization by electron beam, X-ray or UV-ray irradiation is caused to occur. The monomers to be used in this case may include the following: 45

④ $R_1 - \text{CH}_2 - nX - R_2$ $10 \leq n \leq 25$

$X = -\text{COO}-, -\text{CONH}-, -\text{OCO}-$

$R_1 = -\text{CH}_3, -\text{CH}=\text{CH}_2$

$R_2 = -\text{H}, -\text{CH}=\text{CH}_2, -\text{C}(\text{CH}_3)=\text{CH}_2, -\text{CH}_2\text{CH}=\text{CH}_2$
(with proviso that R_2 cannot be $-\text{H}$ where R_1 is $-\text{CH}_3$)

⑤ $\text{H}-(\text{CH}_2)_n \text{C}\equiv\text{CC}-\text{C}\equiv\text{C}-(\text{CH}_2)_m \text{X}-R_2$ $0 \leq m, n, 10 \leq m+n \leq 25$ 55

$\text{X} = -\text{COO}, -\text{CONH}, -\text{OCO}-$

$R_2 = -\text{H}, -\text{CH}=\text{CH}_2, -\text{C}(\text{CH}_3)=\text{CH}_2, -\text{CH}_2\text{CH}=\text{CH}_2$ 60

5) The method in which direct recording is effected through change in configuration or configuration of the compound by irradiation of visible light or UV-ray. For example, there may be employed:

- a) spirobifluorene, fulgide or azobenzene derivatives having photochromic property;
- b) dyes in which the associated state is changed, for example, melocyanine compounds, cyanine compound, or squarilium and croconic methine compounds, particularly azulene type compounds.

The thin film structure change of an LB film, etc. as mentioned here may sometimes occur alone, but in many cases some effects will generally occur associatedly.

As the electrode for laminating a thin film such as an LB film, etc. as described above, all conductors having conductivity of 10^{-6} ($\Omega \cdot \text{cm}$)⁻¹ or higher can be used. More specifically, with the use of a metal plate such as Au, Pt, Pd, Ag, Al, or a glass, ceramics, plastic materials having these metals vapor deposited thereon, or semiconductors such as Si (crystalline, amorphous) as the substrate, a thin film such as LB film can be laminated thereon and used as the recording medium.

Example 1
A recording/reproducing device shown in Fig. 1 was employed. As the probe electrode 102, a probe electrode made of platinum was used. This probe electrode 102 is used for controlling the distance (Z) from the surface of the recording layer 101, and its distance (Z) is finely controlled by a piezoelectric element so that the current may be controlled to be constant. Further, the fine control mechanism 107 is designed so that fine movement control may be possible also in the plane (X,Y) direction. However, all of these are known techniques. Also, the probe electrode 102 can be used for direct recording, regeneration and erasing. The recording medium is placed on the XY stage 114 with high precision and can be moved to any desired position.

Next, the experiments of recording, reproduction and erasing by use of an LB film (8 layers) of squarilium-bis-6-octylazulene (hereinafter abbreviated as SOAZ) formed on the electrode 103 formed of Au are described in detail.

A recording medium 1 having a recording layer with 8 built-up SOAZ layers was placed on the XY stage 114, and first the position of the probe electrode 102 was determined and fixed firmly. Between the Au electrode (the ground side) 103 and the probe electrode 102, a voltage of -3.0 V was applied, and the distance (Z) between the probe electrode 102 and the recording layer 101 surface was controlled while monitoring the current. Thereafter, the distance from the probe electrode 102 to the surface of the recording layer 101 was changed by controlling the fine control mechanism 107, whereby the current characteristics as shown in Fig. 2 were obtained. It is required that the probe voltage should be controlled so that the probe current I_p for controlling the distance from the probe electrode 102 to the surface of the recording layer 101 may be $10^{-7} \text{ A} \geq I_p \geq 10^{-12} \text{ A}$, preferably $10^{-8} \text{ A} \geq I_p \geq 10^{-10} \text{ A}$.

First, the controlled current was set to be current value of the a region in Fig. 2 (10^{-7} A) -(Condition of probe grounding). When the current value was measured by applying reading voltage of 1.5 V which was a voltage not exceeding the threshold voltage which gives rise to electric memory effect between the probe electrode 102 and the Au electrode 103, OFF state was exhibited at μA or less. Next, after a triangular pulse voltage having the waveform shown in Fig. 3 which is a voltage of or higher than the threshold voltage of V_{th} ON which gives rise to ON state, the current was again measured by applying a voltage of 1.5 V between the electrodes, whereby a current of about 0.7 mA was found to flow, thus indicating the ON state.

Next, after a triangular pulse voltage with a peak voltage of 5 V and a pulse width of 1 μs which is a voltage of or higher than the threshold voltage V_{th} OFF at which the change occurs from the ON state to the OFF state, 1.5 V was again applied, whereby it was confirmed that the current value at this time was returned to OFF state at μA or less.

Next, with the probe current I_p being set at 10^{-9} A (b region in Fig. 2), the distance Z between the probe electrode 102 and the surface of the recording layer 101 was controlled.

While moving the XY stage 114 at a constant interval (1 μ), a pulse voltage (15 Vmax, 1 μs) of ON or higher than the threshold value V_{th} ON having the same waveform as in Fig. 3 was applied to write the ON state. Then by applying a probe voltage of 1.5 V for reading between the probe electrode 102 and the counter-electrode 103, the change in current quantity passing between the ON state region and OFF state region can be directly read or through the servo circuit 106. In this Example, it was confirmed that the probe current passing through the ON state region was found to be changed by 3 digits or more as compared with before recording (or the OFF state region).

Further, as the result of tracing again the recording position by setting the probe voltage at 10 V of the threshold voltage V_{th} OFF or higher, it was also confirmed that all the recorded state was erased to be transited to the OFF state.

Next, by use of the fine control mechanism 107, the resolving power was measured by writing stripes of 1 μ length with various pitches between 0.001 μ and 0.1 μ , and it was found to be 0.01 μ or less.

The SOAZ-LB film used in the above experiments was prepared as described below.
After an optically polished glass substrate (substrate 104) was washed by use of a neutral detergent and Trichlene, Cr was deposited as the subbing layer by the vacuum deposition method to a thickness of 50 Å, and further Au was vapor deposited by the same method to 400 Å to form a subbing electrode (Au electrode 103).

Next the chloroform solution containing SOAZ dissolved at a concentration of 0.2 mg/ml was spread over an aqueous phase of 20°C to form a monomolecular film on the water surface. After evaporation of the solvent, the surface pressure of such monomolecular film was enhanced to 20 mN/m, and further while this was maintained to be constant, the above electrode substrate was dipped gently at a speed of 5 mm/min. So as to transverse across the water surface, and further withdrawn to have two layers of Y-form monomolecular film

built up. By repeating appropriate times of this operation, 6 kinds of 2, 4, 8, 12, 20 and 30 layers of built-up films were formed on the above substrate and used for recording and reproducing experiments. The evaluation results are shown in Table 1.

Evaluation was performed overall from the recording and erasing characteristics after applying the pulse and the erasing voltage, further the ratio of the current value under the recording state to that of the erased state (ON/OFF) and the resolving ability, and those with particularly good results were rated as A, those with excellent results as B, and those with relatively somewhat lower results as compared with other as C.

Example 2

The experiments were conducted in the same manner as in Example 1 except for using t-butyl derivative of lutetherium diphthalocyanine [LuH(Pc)₂] in place of the SOAZ recording medium used in Example 1. The results are summarized in Table 1. It was found that writing and reading of record could be done at sufficient S/N ratio as in the case of SOAZ.

The built-up conditions of t-butyl derivative of LuH(Pc)₂ are shown below.

Solvent: chloroform/trimethylbenzene/acetone (1/1/2)

Concentration: 0.5 mg/ml

Aqueous phase: pure water, water temperature 20°C

Surface pressure: 20 mN/m, vertical moving speed of substrate 3mm/min.

Examples 3 - 9

Recording media were prepared by use of the substrate electrode materials and the dye compounds shown in Table 2, and the same experiments as in Examples 1 and 2 were conducted with the controlled current value of the probe current set at 10⁻⁹ A to obtain the results shown in Table 2. As shown by the mark B in the Table, recording and reproduction could be done at sufficient resolving power and ON/OFF ratio for all of the samples.

The built-up number of the dye LB film was all two layers. Also, the Pt electrode was vapor deposited by use of the EB method, and ITO by the sputtering method, respectively.

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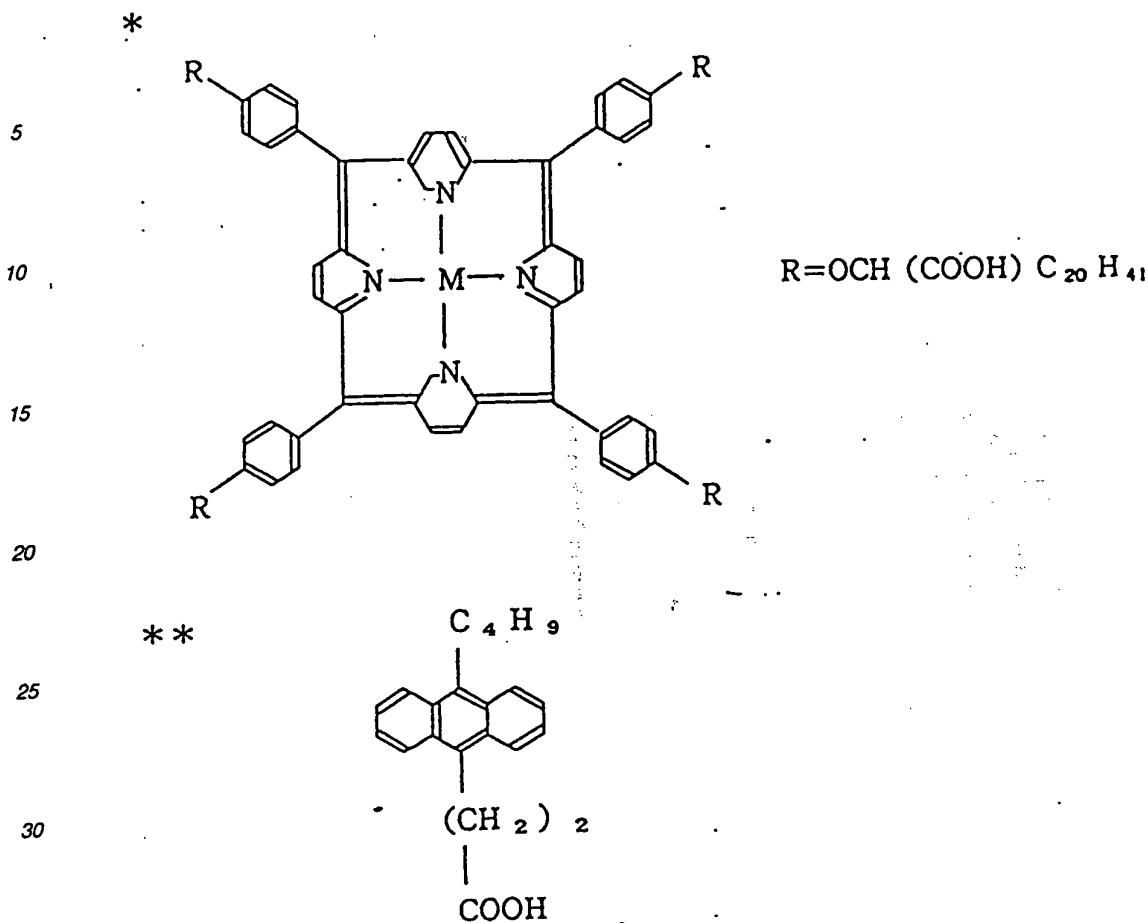
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Table 2

Example	Substrate Electrode	Dye Compound	Recording Reproducibility	Resolving Power
3	Pt (100 Å)	SOAZ	O	Not more than 0.01 μ
5	Cr/Au (50 Å / 400 Å)	Tetraphenylporphyrine derivative *	O	Not more than 0.05 μ
4	ITO (1000 Å)	SOAZ	O	Not more than 0.03 μ
6	Cr/Au (50 Å / 400 Å)	Anthracene derivative **	O	Not more than 0.1 μ
7	Cr/Au (50 Å / 400 Å)	Docosylpyradinium-tetracyanoquinodimethane	O	Not more than 0.01 μ
8	Cr/Au (50 Å / 400 Å)	Pentacos-10,12-dienoic acid	O	Not more than 0.01 μ
9	Cr/Au (50 Å / 400 Å)	Bacteriorhodopsin ***	O	Not more than 0.05 μ



*** violet film extracted from a cultured
product obtained by culturing a highly halophilic
bacterium according to the known method.

In the Examples as described above, the LB method was employed for formation of the dye recording layer, but any film forming method can be used without limitation to the LB method, provided than an extremely thin film can be prepared, and specifically the vacuum vapor deposition method such as MBE, CVD method, etc. may be included.

Applicable materials are not limited to only organic compounds, but inorganic materials such as chalcogenide compounds, etc. are also applicable.

Further, it is also possible to use an integration of the electrode and the recording layer by use of a semiconductor as the electrode on the recording medium side.

The present invention is not limitative of the substrate material, its shape and surface structure at all.

Example 10

A recording/reproducing device shown in Fig. 1 was employed. As the probe electrode 102, a probe electrode made of platinum was used. This probe electrode 102 is used for controlling the distance (Z) from the surface of the recording layer 101, and its distance (Z) is finely controlled by a piezoelectric element so that the current may be controlled to be constant. Further, the fine control mechanisms 107 is designed so that fine control may be possible also in the plane (X,Y) direction. However, all of these are known techniques. Also, the probe electrode 102 can be used for direct recording, regeneration and erasing. The recording medium is placed on the XY stage 114 with high precision and can be moved to any desired position.

Next, the experiments of recording, reproduction and erasing by use of a chalcogenide glass represented by the composition formula $Si_{16}Ge_{14}As_5Te_{65}$ (the subscripts correspond to atomic%) (film thickness 2000 Å) formed on the electrode 103 formed of Au are described in detail.

A recording medium 1 having a recording layer 101 of the above chalcogenide glass having a thickness of 2000 Å was placed on the XY stage 114. Between the Au electrode (the ground side) 103 and the probe electrode 102, a voltage of 1.0 V was applied, and the distance (Z) between the probe electrode 102 and the recording layer 101 surface was controlled while monitoring the current. Thereafter, the fine control mechanism 107 was controlled so that the probe current I_p became 10^{-9} A.

It is required that the probe voltage should be controlled so that the probe current I_p for controlling the distance from the probe electrode 102 to the surface of the recording layer 101 may be $10^{-7} \text{ A} \geq I_p \geq 10^{-12} \text{ A}$, preferably $10^{-8} \text{ A} \geq I_p \geq 10^{-10} \text{ A}$.

While moving the XY stage 114 at a constant interval (1 μ), a rectangular pulse voltage (20 Vmax, 0.1 μS) of or higher than the threshold value $V_{th\ ON}$ was applied to give rise to a low resistance state (ON state). Then, by applying a probe voltage of 1.0 V for reading between the probe electrode 102 and the counter-electrode 103, the change in current quantity passing between the ON state region and OFF state region can be directly read or through the servo circuit 106. In this Example, it was confirmed that the probe current passing through the ON state region was found to be changed by 2 digits or more as compared with before recording (or the OFF state region).

Further, as the result of tracing again the recording position while applying a rectangular pulse voltage (50 Vmax, 10 μS) of or higher than the threshold voltage $V_{th\ OFF}$ on the probe electrode, it was also confirmed that all the recorded state was erased to be transited to the OFF state. Erasing of recording is also possible by the optical method.

Next, by use of the fine control mechanism 107, the resolving power was measured by writing stripes of 1 μ length with various pitches between 0.01 μ and 1 μ, and it was found to be 0.1 μ or less.

The chalcogenide glass used in the above experiments was prepared as described below.

After an optically polished glass substrate (substrate 104) was washed by use of a neutral detergent and Trichlene, Cr was deposited as the subbing layer by the vacuum deposition method to a thickness of 50 Å, and further Au was vapor deposited by the same method to 400 Å to form a subbing electrode (Au electrode 103).

Next, an amorphous semiconductor represented by the atomic composition ratio of $\text{Si}_{16}\text{Ge}_{14}\text{As}_5\text{Te}_{65}$ was vapor deposited to a film thickness of 2000 Å by the vacuum vapor deposition method known in the art and used as the recording medium.

Example 11

The same experiment as in Example 10 was conducted except for using $\text{Ge}_{15}\text{Te}_{81}\text{Sb}_2\text{S}_2$ in place of $\text{Si}_{16}\text{Ge}_{14}\text{As}_5\text{Te}_{65}$ used in Example 10. It was found that writing and reading of record could be done at sufficient S/N ratio similarly as in Example 1.

Example 12

The same recording and reproducing experiment as in Example 1, except for using CuTCNQF_4 in place of the chalcogenide glass recording medium used in Examples 10 and 11. A rectangular pulse of 2 Vmax, 10 ns was used as the application voltage for recording, and the application voltage for control of the probe current was made 0.1 V. As the result, recording and reproduction could be done at sufficient S/N ratio similarly as in Example 1. The method for preparation of the CuTCNQF_4 recording medium is described below.

After an optically polished glass substrate was washed, Cu was deposited to 2000 Å according to the vacuum vapor deposition method to provide an electrode. Further, Cu and TCNQF_4 were co-deposited by the vacuum vapor deposition method to deposit a CuTCNQF_4 layer to 2000 Å (substrate temperature; room temperature). At this time, heating was effected by passing current value previously set so that the vapor deposition speed may become about Cu, 5 Å/s; TCNQF_4 , 20 Å/s. As the result, it was confirmed that a blue film by formation of CuTCNQF_4 was deposited.

Example 13

After an electrode was formed by vacuum vapor deposition of Cr to a film thickness of 500 Å on an optically polished glass substrate, an amorphous silicon film of p^+ type with a thickness of 1000 Å was formed. The preparation conditions at that time were as follows:

Introduced gases: $\text{B}_2\text{H}_6/\text{SiH}_4$ ($N_{\text{BH}}/N_{\text{SiH}} = 10^{-1}$) (diluted with H_2 gas to 0.025 mol%)

rf power: 0.01 W/cm²

Pressure: 0.5 torr

Substrate temperature: 300 °C

Deposition speed: 30 Å/min.

Next, after the superfluous starting gases were discharged, new starting gases were fed to deposit a n-type amorphous silicon to 5000 Å. The preparation conditions were as follows.

Introduced gases: PH_3/SiH_4 ($N_{\text{PH}}/N_{\text{SiH}} = 5 \times 10^{-3}$) (diluted with H_2 gas to 0.05 mol%)

rf power: 0.01 W/cm²

Pressure: 0.5 torr

Substrate temperature: 300 °C

Deposition speed: 40 Å/min.

Also, after the starting gases were discharged, SiH_4 diluted with H_2 gas to 0.05 mol% was introduced into the chamber, and an i-phase amorphous silicon was deposited to 1000 Å under otherwise the same conditions.

By use of the recording medium as prepared above, the same recording and reproduction were effected in the same manner as in Example 10. As the result, recording and reproduction could be done with sufficient S/N ratio exhibited. For recording, reproduction and erasing, the following voltages were applied.

For recording: 20 V
5 For reproduction: 0.5 V
For erasing: -5V

Having described about the methods for various recording media in the above Examples, any film forming method capable of preparing an extremely uniform film can be used and the method of the present invention is not limitative. The present invention is not also limitative of the substrate material, its shape and surface structure at all.

Example 14

A recording/reproducing device shown in Fig. 10 was employed. As the probe electrodes 1002a, b, c, three tungsten probe electrodes 3 were employed. The probe electrodes 1002a, b, c were used for controlling the distance (Z) from the surface of the recording layer 101, and its distance (Z) is finely controlled by a piezoelectric element so that the current may be controlled to be constant. Further, the fine control mechanism 1007 is designed so that fine control may be possible also in the plane (X,Y) direction. However, all of these are known techniques. Also, the probe electrodes 1002a, b, c can be used for direct recording, reproduction and erasing. The recording medium is placed on the XY stage 1014 with high precision and can be moved to any desired position.

Next, the experiments of recording, reproduction and erasing by use of an LB film (8 layers) of squarilium-bis-6-octylazulene (hereinafter abbreviated as SOAZ) formed on the electrode 1003 formed of Au are described in detail.

A recording medium 1 having a recording layer 101 with 8 built-up SOAZ layers was placed on the XY stage 1014, and first the positions of the probe electrodes 1002a, b, c were determined and fixed firmly. Between the Au electrode (the ground side) 1003 and the probe electrode 1002, a voltage of -3.0 V was applied, and the distance (Z) between the probe electrode 1002 and the recording layer 101 surface was controlled while monitoring the current. Thereafter, the distance from the probe electrode 1002 to the surface of the recording layer 101 was changed by controlling the fine control mechanism 1007, whereby the current characteristics as shown in Fig. 2 were obtained. It is required that the probe voltage should be controlled so that the probe current I_p for controlling the distance from the probe electrode 1002 to the surface of the recording layer 101 may be $10^{-7}A \geq I_p \geq 10^{-12}A$, preferably $10^{-8}A \geq I_p \geq 10^{-10}A$.

First, the controlled current was set to the current value of the a region in Fig. 2 ($10^{-7}A$) -(Condition of probe grounding). When the current value was measured by applying reading voltage of 1.5 V which was a voltage not exceeding the threshold voltage which gives rise to electric memory effect between the probe electrode 1002 and the Au electrode 1003, OFF state was exhibited at μA or less. Next, after a triangular pulse voltage having the waveform shown in Fig. 3 which is an voltage of or higher than the threshold voltage $V_{th\ ON}$ which gives rise to ON state, the current was again measured by applying a voltage of 1.5 V between the electrodes, whereby a current of about 0.7 mA was found to flow, thus indicating the ON state.

Next, after the triangular pulse voltage with a peak voltage of 5 V and a pulse width of 1 μS which is a voltage of or higher than the threshold voltage $V_{th\ OFF}$ at which the change occurs from the ON state to the OFF state, 1.5 V was again applied, whereby it was confirmed that the current value at this time was returned to OFF state at μA or less.

Next, with the probe current I_p being set at $10^{-9}A$ (b region in Fig. 2), the distance Z between the prob electrode 1002a, b, c and the surface of the recording layer 101 was controlled.

While moving the XY stage slowly along the Y-axis under application of a triangular pulse voltage having the waveform as shown in Fig. 3 which is a voltage of the threshold voltage $V_{th\ ON}$ or high at which the ON state occurs at the three probes, the track signal Y track was recorded (Fig. 11A)

The probes 1002 a, b and c were returned to the original positions, then while applying a triangular pulse voltage having the waveform as shown in Fig. 3 which is a voltage of the threshold voltage $V_{th\ ON}$ or higher at which the ON state occurs at the two probes (1002-a, c) along the X-axis, track signals along the X-axis were recorded (Fig. 11B).

The remaining one probe (1002-b) wrote the ON state by applying a pulse voltage (15 Vmax, 1 μS) of the threshold voltage $V_{th\ ON}$ or higher having the same waveform as in Fig. 3 at the predetermined position of the timing signal, and also the data were recorded at the remaining sites by use of the same method.

Next, the probe 1002-a was moved along the Y-axis to the track recorded with the probe 1002-c, and the same operation as described above was conducted. At this time, only the probe 1001a performs reading of the track signal. Subsequently, this operation was repeated until a recording medium having the track signals and the data recorded thereon was prepared (Fig. 11C).

Reading can be done by applying a prob voltage of 1.5 V for reading between the probe electrode 1002-b and the counter-electrode 1003, and reading directly the change in current quantity passing between the ON state region and OFF state region or through the servo circuit 1006. In this Example, it was confirmed that the probe current passing through the ON state region was found to be changed by 3 digits or more as compared with that before recording (or the OFF state region).

Further, as the result of tracing again the recording position by setting the probe voltage at 10 V of the

threshold voltage V_{th} OFF or higher, it was also confirmed that all the recorded state was erased to be transited to the OFF state.

Next, by use of the fine control mechanism 1007, the resolving power was measured by writing stripes of 1μ length with various pitches between 0.001μ and 0.1μ , and it was found to be 0.01μ or less.

The SOAZ-LB film used in the above experiments was prepared as described below.

After an optically polished glass substrate (substrate 1004) was washed by use of a neutral detergent and Trichlene, Cr was deposited as the subbing layer by the vacuum deposition method to a thickness of 50 \AA , and further Au was vapor deposited by the same method to 400 \AA to form a subbing electrode (Au electrode 1003).

Next, a chloroform solution containing SOAZ dissolved at a concentration of 0.2 mg/ml was spread over an aqueous phase of 20°C to form a monomolecular film on the water surface. After evaporation of the solvent, the surface pressure of such monomolecular film was enhanced to 20 mN/m , and further while this was maintained to be constant, the above electrode substrate was dipped gently at a speed of 5 mm/min . so as to transverse across the water surface, and further withdrawn to have two layers of Y-form monomolecular film built up. By repeating appropriate times of this operation, 6 kinds of 2, 4, 8, 12, 20 and 30 layers of built-up films were formed on the above substrate and used for recording and reproducing experiments. The evaluation results are shown in Table 3.

Evaluation was performed overall from the recording and erasing characteristics after applying the pulse and the erasing voltage, further the ratio of the current value under the recording state to that of the erased state (ON/OFF) and the resolving power, and those with particularly results were rated as A, those with good results as B, and those with relatively somewhat lower results as compared with others as C.

Example 15

The experiments were conducted in the same manner as in Example 14 except for using t-butyl derivative of lutheum diphthalocyanine [$\text{LuH}(\text{Pc})_2$] in place of the SOAZ recording medium used in Example 14. The results are summarized in Table 3. It was found that writing and reading of record could be done at sufficient S/N ratio as in the case of SOAZ.

The built-up conditions of t-butyl derivative of $\text{LuH}(\text{Pc})_2$ are shown below.

Solvent: chloroform/trimethylbenzene/acetone (1/1/2)

Concentration: 0.5 mg/ml

Aqueous phase: pure water, water temperature 20°C

Surface pressure: 20 mN/m , vertical moving speed of substrate 3 mm/min .

Examples 16 - 22

Recording media were prepared by use of the substrate electrode materials and the dye compounds shown in Table 4, and the same experiments as in Examples 14 and 15 were conducted with the controlled current value of the probe current set at 10^{-9} A to obtain the results shown in Table 4. As shown by the mark B in the Table, recording and reproduction could be done at sufficient resolving power and ON/OFF ratio for all of the samples.

The built-up number of the dye LB film was all two layer. Also, the Pt electrode was vapor deposited by use of the EB method, and ITO by the sputtering method, respectively.

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Table 3

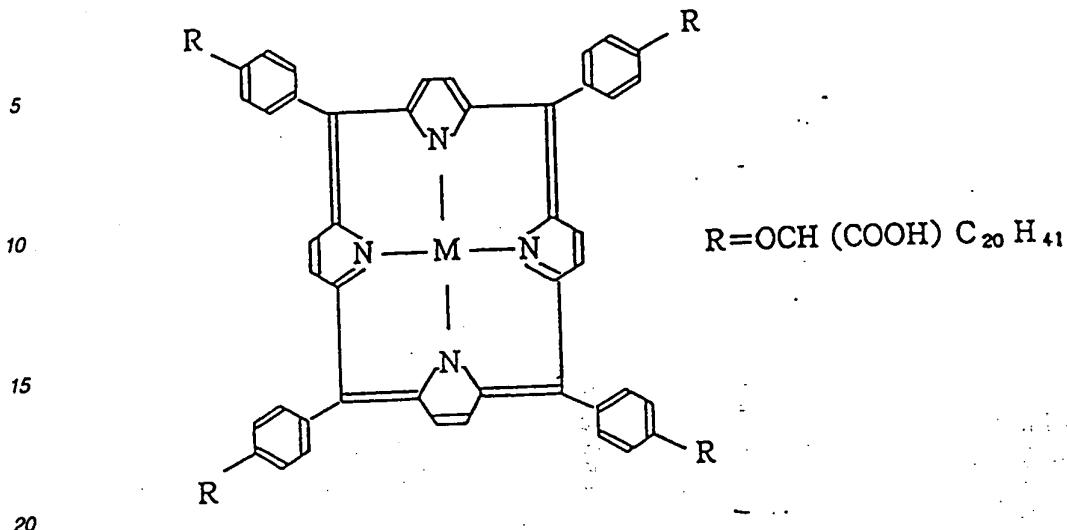
Organic Compound	Built-up Number	a Region		b Region		Resolving Power	
		Recording Characteristic	ON/OFF Ratio	Recording Characteristic	ON/OFF Ratio	Erasability	Erasability
SOA2	2	A	B	A	A	A	A
	4	A	B	A	A	A	A
	8	A	A	A	A	A	A
	12	A	A	A	A	A	A
	20	B	A	A	B	A	A
	30	B	A	A	C	A	A
LuH (Pc)	2	A	C	A	B	A	A
	4	A	B	A	A	A	A
	8	A	B	A	A	A	A
	12	A	A	A	A	A	A
	20	B	A	A	C	A	A
	30	C	A	A	C	A	A

Table 4

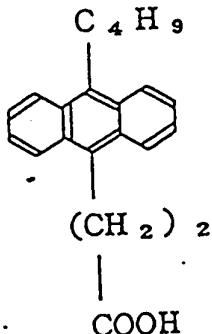
Example	Substrate Electrode	Dye Compound	Recording Reproduc- ibility	Resolving Power
16	Pt (1 0 0 Å)	SOAZ	O	Not more than 0.01 μ
17	Cr / Au (50 Å / 400 Å)	Tetraphenylporphyrine derivative *	O	Not more than 0.05 μ
18	ITO (1000 Å)	SOAZ	O	Not more than 0.03 μ
19	Cr / Au (50 Å / 400 Å)	Anthracene derivative **	O	Not more than 0.1 μ
20	Cr / Au (50 Å / 400 Å)	Docosylpyradinium- tetracyanoquinodimethane	O	Not more than 0.01 μ
21	Cr / Au (50 Å / 400 Å)	Pentacosa-10,12-diynoic acid	O	Not more than 0.01 μ
22	Cr / Au (50 Å / 400 Å)	Bacteriorhodopsin ***	O	Not more than 0.05 μ

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* *



40 *** violet film extracted from a cultured
product obtained by culturing a highly halophilic
bacterium according to the known method.
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Example 23

Example 23 When the same experiments were conducted by use of the devices shown in Fig. 10A-B, and devices shown in Fig. 10A-C, the same results were obtained.

In the Examples as described above, the LB method was employed for formation of the dye recording layer, but any film forming method can be used without limitation to the LB method, provided that an extremely thin film can be prepared, and specifically the vacuum vapor deposition method such as an MBE method, a CVD method, etc. may be included.

Applicable materials are not limited to only other organic compounds, but inorganic materials such as chalcogenide compounds, etc. are also applicable.

Further, it is also possible to use an integration of the electrode and the recording layer by using an insulator as the electrode on the recording medium side.

Example 24

Example 24
A recording/reproducing device shown in Fig. 1 was employed. As the probe electrode 102, a probe electrode made of platinum was used. This probe electrode 102 is used for controlling the distance (Z) from

the surface of the recording layer 101, and its distance (Z) is finely controlled by a piezoelectric element so that the current may be controlled to be constant. Further, the fine control mechanism 107 is designed so that fine control may be possible also in the plane (X, Y) direction. However, all of these are known techniques. Also, the probe electrode 102 can be used for direct recording, regeneration and erasing. The recording medium is placed on the XY stage 114 with high precision and can be moved to any desired position.

The experiments of recording, reproduction and erasing by use of an LB film (8 layers) of squarilium-bis-6-octylazulene (hereinafter abbreviated as SOAZ) formed on the electrode 103 formed of Au are described below in detail.

A recording medium 1 having a recording layer with 8 built-up SOAZ layers was placed on the XY stage 114, and first the position of the probe electrode 102 was determined and fixed firmly. Between the Au electrode (the ground side) 103 and the probe electrode 102, a voltage of -3.0 V was applied, and the distance (Z) between the probe electrode 102 and the recording layer 101 surface was controlled while monitoring the current. Thereafter, the distance from the probe electrode 102 to the surface of the recording layer 101 was changed by controlling the fine control mechanism 107, whereby the current characteristics as shown in Fig. 2 were obtained. It is required that the probe voltage should be controlled so that the probe current I_p for controlling the distance from the probe electrode 102 to the surface of the recording layer 101 may be $10^{-7} \text{ A} \geq I_p \geq 10^{-12} \text{ A}$, preferably $10^{-8} \text{ A} \geq I_p \geq 10^{-10} \text{ A}$.

First, the controlled current was set to be current value of the a region in Fig. 2 (10^{-7} A) -(Condition of probe grounding). When the current value was measured by applying reading voltage of 1.5 V which was a voltage not exceeding the threshold voltage which gives rise to electric memory effect between the probe electrode 102 and the Au electrode 103, OFF state was exhibited at μA or less. Next, after a triangular pulse voltage having the waveform shown in Fig. 3 which is a voltage of or higher than the threshold voltage of $V_{th\ ON}$ which gives rise to ON state, the current was again measured by applying a voltage of 1.5 V between the electrodes, whereby a current of about 0.7 mA was found to be flow, thus indicating the ON state.

Next, after a triangular pulse voltage with a peak voltage of 5 V and a pulse width of 1 μs which is a voltage of or more of the threshold voltage $V_{th\ OFF}$ at which the change occurs from the ON state to the OFF state, 1.5 V was again applied, whereby it was confirmed that the current value at this time was returned to OFF state at μA or less.

Next, with the probe current I_p being set at 10^{-9} A (b region in Fig. 2), the distance Z between the probe electrode 102 and the surface of the recording layer 101 was controlled.

While moving the XY stage 114 at a constant interval (1 μ), a pulse voltage (15 Vmax, 1 μs) of the threshold value $V_{th\ ON}$ or higher having the same waveform as in Fig. 3 was applied to write the ON state. Then, by applying a probe voltage of 1.5 V for reading between the probe electrode 102 and the counter-electrode 103, the change in current quantity passing between the ON state region and OFF state region can be directly read or through the servo circuit 106. In this Example, it was confirmed that the probe current passing through the ON state region was found to be changed by 3 digits or more as compared with that before recording (or the OFF state region).

Further, as the result of tracing again the recording position by setting the probe voltage at 10 V of the threshold voltage $V_{th\ OFF}$ or higher, it was also confirmed that all the recorded state was erased to be transited to the OFF state.

Next, by use of the fine control mechanism 107, the resolving power was measured by writing stripes of 1 μ length with various pitches between 0.001 μ and 0.1 μ , and it was found to be 0.01 μ or less.

The SOAZ-LB film used in the above experiments was prepared as described below.

After an optically polished glass substrate (substrate 104) was washed by use of a neutral detergent and Trichlene, Cr was deposited as the subbing layer by the vacuum deposition method to a thickness of 50 \AA , and further Au was vapor deposited by the same method to 400 \AA to form a subbing electrode (Au electrode 103).

Next, a chloroform solution containing SOAZ dissolved at a concentration of 0.2 mg/ml was spread over an aqueous phase of 20°C to form a monomolecular film on the water surface. After evaporation of the solvent, the surface pressure of such monomolecular film was enhanced to 20 mN/m, and further while this was maintained to be constant, the above electrode substrate was dipped gently at a speed of 5 mm/min. so as to transverse across the water surface, and further withdrawn to have two layers of Y-form monomolecular film built up. By repeating appropriate times of this operation, 6 kinds of 2, 4, 8, 12, 20 and 30 layers of built-up films were formed on the above substrate and used for recording and reproducing experiments. The evaluation results are shown in Table 1.

Evaluation was performed overall from the recording and erasing characteristics after applying the pulse and the erasing voltage, further the ratio of the current value under the recording state to that of the erased state (ON/OFF) and the resolving power, and those with particularly excellent results were rates as A, those with good results as B, and those with relatively somewhat lower results as compared with others as C.

Example 25

The experiments were conducted in the same manner as in Example 1 except for using t-butyl derivative of lutetium diphthalocyanine [LuH(Pc)₂] in place of the SOAZ recording medium used in Example 24. The results are summarized in Table 5. It was found that writing and reading of record could be done at sufficient S/N ratio as in the case of SOAZ.

The built-up conditions of t-butyl derivative of LuH(Pc)₂ are shown below.

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Solvent: chloroform/trimethylbenzene/acetone (1/1/2)

Concentration: 0.5 mg/ml

Aqueous phase: pure water, water temperature 20°C

Surface pressure: 20 mN/m, vertical moving speed of the substrate 3 mm/min.

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Examples 26 - 32

Recording media were prepared by use of the substrate electrode materials and the dye compounds shown in Table 6, and the same experiments as in Examples 24 and 25-were conducted with the controlled current value of the probe current set at 10^{-9} A to obtain the results shown in Table 6. As shown by the mark B in the

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Table, recording and reproduction could be done at sufficient resolving power and ON/OFF ratio for all of the samples.

The built-up number of the dye LB film was all two layers. Also, the Pt electrode was vapor deposited by use of the EB method, and ITO by the sputtering method, respectively.

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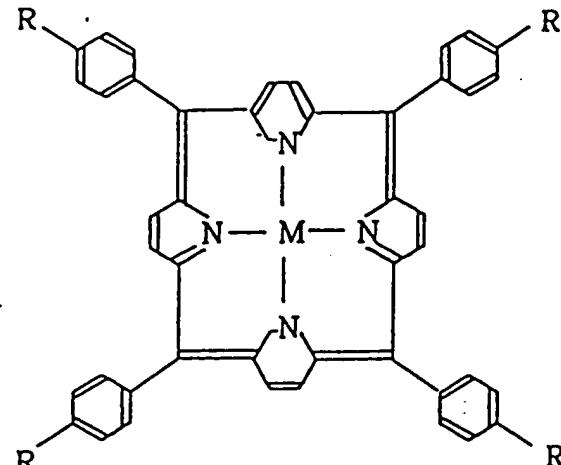
Table 5

Organic Compound	Built-up Number	a Region		b Region		Resolving Power	
		Recording Characteristic	ON/OFF Ratio	Erasability	Recording Characteristic	ON/OFF Ratio	Erasability
SOAZ	2	A	B	A	A	A	Not more than 0.01 μ
	4	A	B	A	A	A	"
	8	A	A	A	A	A	"
	12	A	A	A	A	A	"
	20	B	A	A	B	A	Not more than 0.1 μ
	30	B	A	A	C	A	"
LuH (Pc)	2	A	C	A	A	B	Not more than 0.03 μ
	4	A	B	A	A	A	"
	8	A	B	A	A	A	"
	12	A	A	A	A	A	"
	20	B	A	A	C	A	Not more than 0.1 μ
	30	C	A	A	C	A	"

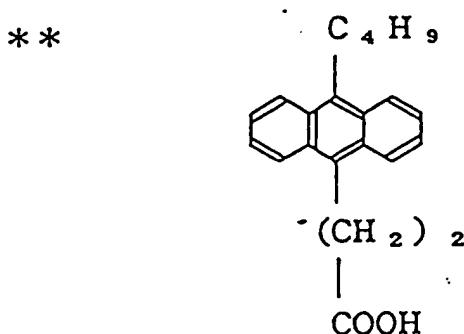
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Table 6

Example	Substrate Electrode	Dye Compound	Recording Reproduc- ibility	Resolving Power
26	Pt (100 Å)	SOAZ	O	Not more than 0.01 μ
27	Cr/Au (50 Å / 400 Å)	Tetraphenylporphyrine derivative *	O	Not more than 0.05 μ
28	ITO (1000 Å)	SOAZ	O	Not more than 0.03 μ
29	Cr/Au (50 Å / 400 Å)	Anthracene derivative **	O	Not more than 0.1 μ
30	Cr/Au (50 Å / 400 Å)	Docosylpyradinium- tetracyanoquinodimethane	O	Not more than 0.01 μ
31	Cr/Au (50 Å / 400 Å)	Pentacosa-10,12-diynoic acid	O	Not more than 0.01 μ
32	Cr/Au (50 Å / 400 Å)	Bacteriorhodopsin ***	O	Not more than 0.05 μ



$R = OCH_2(COOH)C_{20}H_{41}$



*** violet film extracted from a cultured product obtained by culturing a highly halophilic bacterium according to the known method.

In the Examples as described above, the LB method was employed for formation of the dye recording layer, but any film forming method can be used without limitation to the LB method, provided that an extremely thin film can be prepared, and specifically the vacuum vapor deposition method such as an MBE, an CVD method, etc. may be included.

Applicable materials are not limited to only organic compounds, but inorganic materials such as chalcogenide compounds, etc. are also applicable.

Further, it is also possible to use an integration of the electrode and the recording layer by use of a semiconductor as the electrode on the recording medium side.

The present invention is not limitative of the substrate material, its shape and surface structure at all.

Example 33

A recording/reproducing device shown in Fig. 1 was employed. As the probe electrode 102, a probe electrode made of platinum was used. This probe electrode 102 is used for controlling the distance (Z) from the surface of the recording layer 101, and its distance (Z) is finely controlled by a piezoelectric element so that the current may be controlled constant. Further, the fine control mechanism 107 is designed so that fine control may be possible also in the plane (X,Y) direction. However, all of these are known techniques. Also, the probe electrode 102 can be used for direct recording, regeneration and erasing. The recording medium is placed on the XY stage with high precision and can be moved to any desired position.

Next, the experiments of recording, reproduction and erasing by use of a chalcogenide glass represented by the composition formula $Si_{16}Ge_{14}As_5Te_{65}$ (the subscripts correspond to atomic%) (film thickness 2000 Å) formed on the electrode 103 formed of Au are described in detail.

A recording medium 1 having a recording layer 101 of the above chalcogenide glass having a thickness of

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2000 Å was placed on the XY stage 114. Between the Au electrode (the ground side) 103 and the probe electrode 102, a voltage of 1.0 V was applied, and the distance (Z) between the probe electrode 102 and the recording layer 101 surface was controlled while monitoring the current. Thereafter, the fine control mechanism 107 was controlled so that the probe current I_p became 10^{-9} A.

5 It is required that the probe voltage should be controlled so that the probe current I_p for controlling the distance from the probe electrode 102 to the surface of the recording layer 101 may be $10^{-7} \text{ A} \geq I_p \geq 10^{-12} \text{ A}$, preferably $10^{-8} \text{ A} \geq I_p \geq 10^{-10} \text{ A}$.

10 While moving the XY stage 114 at a constant interval (1 μ), a rectangular pulse voltage (20 Vmax, 1 μS) of the threshold value V_{th} ON or higher was applied to give rise to a low resistance state (ON state). Then by applying a probe voltage of 1.0 V for reading between the probe electrode 102 and the counter-electrode 103, the change in current quantity passing between the low resistance state region and the high resistance state region can be directly read or through the servo circuit 106. In this Example, it was confirmed that the probe current passing through the ON state region was found to be changed by 2 digits or more as compared with before recording (or the OFF state region).

15 Further, as the result of tracing again the recording position while applying a rectangular pulse voltage (50 Vmax, 10 μS) of or higher than the threshold voltage V_{th} OFF on the probe electrode, it was also confirmed that all the recorded state was erased to be transited to the OFF state. Erasing of recording is also possible by the optical method.

20 Next, by use of the fine control mechanism 107, the resolving power was measured by writing stripes of 1 μ length with various pitches between 0.01 μ and 1 μ, and it was found to be 0.1 μ or less.

The chalcogenide glass used in the above experiments was prepared as described below.

After an optically polished glass substrate (substrate 104) was washed by use of a neutral detergent and Trichlene, Cr was deposited as the subbing layer by the vacuum deposition method to a thickness of 50 Å, and further Au was vapor deposited by the same method to 400 Å to form a subbing electrode (Au electrode 103).

25 Next, an amorphous semiconductor represented by the atomic composition ratio of $\text{Si}_{16}\text{Ge}_{14}\text{As}_5\text{Te}_{65}$ was vapor deposited to a film thickness of 2000 Å by the vacuum vapor deposition method known in the art and used as the recording medium.

Example 34

30 The same experiment as in Example 33 was conducted except for using $\text{Ge}_{15}\text{Te}_{81}\text{Sb}_2\text{S}_2$ in place of $\text{Si}_{16}\text{Ge}_{14}\text{As}_5\text{Te}_{65}$ used in Example 33. It was found that writing and reading of record could be done at sufficient S/N ratio similarly as in Example 33.

Example 35

35 The same recording and reproducing experiment as in Example 33, except for using CuTCNQF_4 in place of the chalcogenide glass recording medium used in Examples 33 and 34. A rectangular pulse of 2 Vmax, 10 ns was used as the application voltage for recording, and the application voltage for control of the probe current was made 0.1 V. As the result, recording and reproduction could be done at sufficient S/N ratio similarly as in Example 33. The resolving power was not more than 0.1 μm. The method for preparation of the CuTCNQF_4 recording medium is described below.

40 After an optically polished glass substrate was washed, Cu was deposited to 2000 Å according to the vacuum vapor deposition method to provide an electrode. Further, Cu and TCNQF_4 were co-deposited by the vacuum vapor deposition method to deposit a CuTCNQF_4 layer to 2000 Å (substrate temperature; room temperature). At this time, heating was effected by passing current value previously set so that the vapor deposition speed may become about $\text{Cu}, 5 \text{ Å/s}; \text{TCNQF}_4, 20 \text{ Å/s}$. As the result, it was confirmed that a blue film by formation of CuTCNQF_4 was deposited.

Example 36

45 After an electrode was formed by vacuum vapor deposition of Cr to a film thickness of 500 Å on an optically polished glass substrate, an amorphous silicon film of p^+ type with a thickness of 1000 Å was formed. The preparation conditions at that time were as follows:

Introduced gases: $\text{B}_2\text{H}_6/\text{SiH}_4$ ($N_{\text{BH}}/N_{\text{SiH}} = 10^{-1}$) (diluted with H_2 gas to 0.025 mol%)

rf power: 0.01 W/cm²

Pressure: 0.5 torr

55 Substrate temperature: 300 °C

Deposition speed: 30 Å/min.

Next, after the superfluous starting gases were discharged, new starting gases were fed to deposit a n-type amorphous silicon to 5000 Å. The preparation conditions were as follows.

Introduced gases: PH_3/SiH_4 ($N_{\text{PH}}/N_{\text{SiH}} = 5 \times 10^{-3}$) (diluted with H_2 gas to 0.05 mol%)

60 rf power: 0.01 W/cm²

Pressure: 0.5 torr

Substrate temperature: 300 °C

Deposition speed: 40 Å/min.

65 Also, after the starting gases were discharged, SiH_4 diluted with H_2 gas to 0.05 mol% was introduced into the chamber, and an i-phase amorphous silicon was deposited to 1000 Å under otherwise the same conditions.

By use of the recording medium as prepared above, the same recording and reproduction were effected. As a result, recording and reproduction could be done with sufficient S/N ratio exhibited. For recording, reproduction and erasing, the following voltages were applied.

For recording: 20 V

For reproduction: 0.5 V

For erasing: -5 V

Having described about the methods for various recording media in the above Examples, any film forming method capable of preparing an extremely uniform film can be used and the method of the present invention is not limitative. The present invention is not also limitative of the substrate material, its shape and surface structure at all.

Example 36A

By use of Au as the electrode 103 shown in Fig. 1, an LB film having two layers of pentacosa-10, 12-dienoic acid (DA12-8) built up as the recording layer on the Au electrode was used.

Such polymerizable recording medium was mounted on ELS-3300 electron beam picture drawing device produced by Elionics Co., and a picture was drawn by use of a lattice pattern generating device shown in Fig. 12A under the conditions of an acceleration voltage of 20 kV, a current value of $1 \times 10^{-9} A$, a stationary spot diameter of $0.4 \mu m$, an exposure time of $0.5 \mu sec/spot$.

The magnification at this time was 50-fold.

Next, under the conditions of an acceleration voltage of 20 kV, a current value of $1 \times 10^{-11} A$, a stationary spot diameter of $0.04 \mu m$, an exposure time of $0.5 \mu sec/spot$, a line pattern in Fig. 12 was similarly drawn within each lattice.

The pattern thus drawn was read by use of a reproducing device shown in Fig. 1. Next, its process is shown.

With the recording medium firmly fixed on the stage, first the position of the probe electrode was determined by visual observation. At a probe voltage set at 2 V, the distance between the probe electrode and the recording medium was controlled so that the probe current became $10^{-9} A$ by controlling the coarse mechanism in the Z direction. After the lattice pattern was first searched by course scanning in the direction within the plane (x, y), the line pattern was read by fine scanning within the plane (x, y), whereby the portion irradiated by the electron beam was polymerized and its film thickness was recognized to be changed (reduced) by about several Å as calculated on the changed amount of servo voltage. Also, the line width read was $0.022 \mu m$ and thus it was found that at least a recording resolving power of about $0.02 \mu m$ could be obtained.

The DA12-8 recording medium used in the above experiment was prepared as described below.

After an optically polished glass substrate was washed clean with a neutral detergent and Trichlene, Cr was deposited to a thickness of 50 \AA as the subbing layer by the vacuum vapor deposition method, and further Au was vapor deposited to 400 \AA to form a subbing electrode. DA12-8 was dissolved in chloroform at a concentration of $1 \times 10^{-3} M$ and $200 \mu l$ of the resultant solution was spread on an aqueous phase ($MnCl_2: 5 \times 10^{-4} M$, $KHCO_3: 5 \times 10^{-5} M$, pH 6.8, water temperature $20^\circ C$).

After evaporation of the solvent, the surface pressure was enhanced to 20 mN/m , and further while maintaining the pressure to be constant, the above electrode substrate was dipped gently so as to transverse across the water surface and further withdrawn to build up two layers of a monomolecular film. The DA12-8 monomolecular built-up film thus formed on the Au electrode was dried on air for 24 hours to provide a recording medium.

Example 37

Entirely the same experiment as in Example 36A was conducted except for using a recording medium having two layers of ω -tricosenic acid on n^+ -Si substrate. However, the exposure time was set at $5 \mu sec/spot$. The line width read was $0.013 \mu m$, and a recording resolving power of about $0.01 \mu m$ may be expected.

The LB film forming conditions of ω -tricosenic acid were as follows.

Solvent: chloroform

Concentration: 1 mg/ml

Aqueous phase: H_2O (pure water), water temperature $20^\circ C$

Surface pressure: 20 mN/m , vertical substrate moving speed 20 mm/min .

Example 38

Entirely the same experiment as in Example 36A was conducted except for using a two-layer built-up film of arachidic acid. However, the exposure time was made $20 \mu sec/spot$. Recording was effected through change in the LB film structure based on generation of heat by electron beam irradiation, and the resolving power was poorer as compared with Examples 36A, 37, with the line width reproduced being $0.062 \mu m$. The LB film forming conditions of arachidic acid were as follows.

Solvent: chloroform

Concentration: 1 mg/ml

Aqueous phase: $CdCl_2: 5 \times 10^{-4} M$, water temperature $20^\circ C$

Surface pressure: 30 mN/m ,

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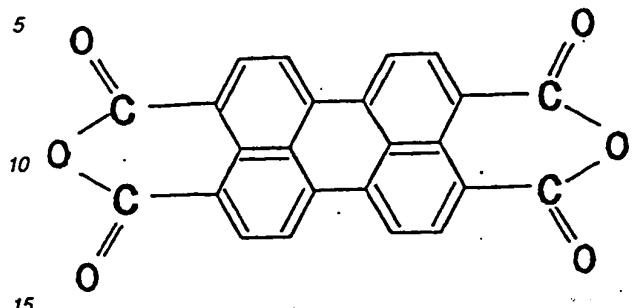
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vertical substrate moving speed 5 mm/min.

Example 39

On the same Au electrode as in Example 36, perylenetetracarboxylic acid anhydride:



was vacuum vapor deposited (vapor deposition speed 5 Å/sec, film thickness 300 Å) to provide a recording medium, and otherwise the same recording and reproducing experiment as in Example 36A was conducted.

As the result of the experiment conducted at an exposure time of 200 μsec/spot, the electron beam irradiated portion was recognized to be blackened. The line width reproduced with a probe voltage of 2V was found to be 0.04 μm.

Example 40

The pattern shown in Fig. 12 was drawn on a p-form <111> wafer substrate (10 ohm-cm) in the same manner as in Example 36 by injecting P⁺ ions by means of a converging ion beam device JIBL produced by Nippon Denshi K.K. The injection conditions were as follows.

Ion source accelerating voltage: 40 kV

Ion beam current: 1 nA

Injected amount: 1.3×10^{14} ions/cm²

Wafer temperature: 300 °C

Next, when the above pattern record was reproduced with a probe voltage of -0.5 V, the line width was found to be 0.083 μm on an average. Thus, it was found that a resolving power of about 0.1 μm or less could be obtained.

As the result of the heat treatment of the above recording medium at 600°C, although the resolving power was reduced to about 0.1 μm, stable reproduced signals could be obtained.

Example 41

The pattern in Fig. 12 was drawn by injecting I⁻ ions by means of the same converging ion beam device in the same manner as in Example 40 on a recording medium having 13 layers of tetraquinodimethane docosylpyridium built up on an optically polished glass substrate.

The injection conditions were ion source acceleration voltage 40 kV, ion beam current 1000 pA, injected amount 5×10^{13} ions/cm², and substrate temperature 20°C.

When the pattern reproduction was effected with a probe voltage of 1 V, the line width was found to be 0.1 μm on an average.

In the Examples as described above, electron beam and ion beam were used as the energy beam, but the energy beam is not limited to these, but electromagnetic waves such as visible light, UV-ray and X-ray, etc. can be also used.

Example 42

A recording/reproducing device shown in Fig. 10 was employed. As the probe electrodes 1002a, b, c, three tungsten probe electrodes were employed. The probe electrodes 1002a, b, c were used for controlling the distance (Z) from the surface of the recording layer 101, and its distance (Z) is finely controlled by a piezoelectric element so that the current may be controlled to be constant. Further, the fine control mechanism 1007 is designed so that fine control may be possible also in the plane (X,Y) direction. However, all of these are known techniques. Also, the probe electrodes 1002a, b, c can be used for direct recording, reproduction and erasing. The recording medium is placed on the XY stage 1014 with high precision and can be moved to any desired position.

Next, the experiments of recording, reproduction and erasing by use of an LB film (8 layers) of squarilium-bis-6-octylazulene (hereinafter abbreviated as SOAZ) formed on the electrode 1003 formed of Au are described in detail.

A recording medium 1 having a recording layer 101 with 8 built-up SOAZ layers was placed on the XY stage 1014, and first the positions of the probe electrodes 1002a, b, c were determined and fixed firmly. Between the Au electrode (the ground side) 1003 and the probe electrodes 1002a, b, c, a voltage of -3.0 V was applied, and the distance (Z) between the probe electrode 1002 and the recording layer 101 surface was controlled while monitoring the current. Thereafter the distance from the probe electrode 1002 to the surface of the recording

layer 101 was changed by controlling the fine control mechanisms 1007, whereby the current characteristics as shown in Fig. 2 were obtained. It is required that the probe voltage should be controlled so that the probe current I_p for controlling the distance from the probe electrode 1002 to the surface of the recording layer 101 may be $10^{-7} \text{ A} \geq I_p \geq 10^{-12} \text{ A}$, preferably $10^{-8} \text{ A} \geq I_p \geq 10^{-10} \text{ A}$.

First, the controlled current was set to the current value of the a region in Fig. 2 (10^{-7} A) -(Condition of probe grounding). When the current value was measured by applying reading voltage of 1.5 V which was a voltage not exceeding the threshold voltage which gives rise to electric memory effect between the probe electrode 1002 and the Au electrode 1003, OFF state was exhibited at μA or less. Next, after a triangular pulse voltage having the waveform shown in Fig. 3 which is a voltage of the threshold voltage of $V_{th \text{ ON}}$ or higher which gives rise to ON state, the current was again measured by applying a voltage of 1.5 V between the electrodes, whereby a current of about 0.7 mA was found to be passed, thus indicating the ON state.

Next, after a triangular pulse voltage with a peak voltage of 5V and a pulse width of $1 \mu\text{s}$ which is a voltage of the threshold voltage $V_{th \text{ OFF}}$ or higher at which the change occurs from the ON state to the OFF state, 1.5 V was again applied, whereby it was confirmed that the current value at this time was returned to OFF state at μA or less.

Next, with the probe current I_p being set at 10^{-9} A (b region in Fig. 2), the distance Z between the probe electrode 1002 and the surface of the recording layer 101 was controlled.

While moving the XY stage slowly along the Y-axis under application of a triangular pulse voltage having the waveform as shown in Fig. 3 which is a voltage of the threshold voltage ON or higher at which the ON state occurs at the three probes, the track signal Y track was recorded (Fig. 11A)

The probes 1002 a, b and c were returned to the original positions, then while applying a triangular pulse voltage having the waveform as shown in Fig. 3 which is a voltage of the threshold voltage $V_{th \text{ ON}}$ or higher at which the ON state occurs at the two probes (1002-a, c) along the X-axis, track signals along the X-axis were recorded (Fig. 11B).

The remaining one probe (1002-b) wrote the ON state by applying a pulse voltage (15 Vmax, $1 \mu\text{s}$) of the threshold voltage $V_{th \text{ ON}}$ or higher having the same waveform as in Fig. 3 at the predetermined position of the timing signal, and also the data were recorded at the remaining sites by use of the same method.

Next, the probe 1002-a was moved along the Y-axis to the track recorded with the probe 1002-c, and the same operation as described above was conducted. At this time, only the probe 1001a performs reading of the track signal. Subsequently, this operation was repeated until a recording medium having the track signals and the data recorded thereon was prepared (Fig. 11C).

Reading can be done by applying a probe voltage of 1.5 V for reading between the probe electrode 1002-b and the counter-electrode 1003, and reading directly the change in current quantity passing between the ON state region and OFF state region or through the servo circuit 1006. In this Example, it was confirmed that the probe current passing through the ON state region was found to be changed by 3 digits or more as compared with before recording (or the OFF state region).

Further, as the result of tracing again the recording position by setting the probe voltage at 10 V of the threshold voltage $V_{th \text{ OFF}}$ or higher, it was also confirmed that all the recorded state was erased to be transited to the OFF state.

Next, by use of the fine control mechanism 1007, the resolving power was measured by writing stripes of 1μ length with various pitches between 0.001μ and 0.1μ , and it was found to be 0.01μ or less.

The SOAZ-LB film used in the above experiments was prepared as described below.

After an optically polished glass substrate (substrate 1004) was washed by use of a neutral detergent and Trichlene, Cr was deposited as the subbing layer by the vacuum deposition method to a thickness of 50 \AA , and further Au was vapor deposited by the same method to 400 \AA to form a subbing electrode (Au electrode 1003).

Next, a chloroform solution containing SOAZ dissolved at a concentration of 0.2 mg/ml was spread over an aqueous phase of 20°C to form a monomolecular film on the water surface. After evaporation of the solvent, the surface pressure of such monomolecular film was enhanced to 20 mN/m , and further while this was maintained to be constant, the above electrode substrate was dipped gently at a speed of 5 mm/min . so as to transverse across the water surface, and further withdrawn to have two layers of Y-form monomolecular film built up. By repeating appropriate times of this operation, 6 kinds of 2, 4, 8, 12, 20 and 30 layers of built-up films were formed on the above substrate and used for recording and reproducing experiments. The evaluation results are shown in Table 7.

Evaluation was performed overall from the recording and erasing characteristics after applying the pulse and the erasing voltage, further the ratio of the current value under the recording state to that of the erased state (ON/OFF) and the resolving power, and those with particularly excellent results were rated as A, those with good results as B, and those with relatively somewhat lower results as compared with others as C.

Example 43

The experiments were conducted in the same manner as in Example 42 except for using t-butyl derivative of lutethium diphthalocyanine [$\text{LuH}(\text{Pc})_2$] in place of the SOAZ recording medium used in Example 42. The results are summarized in Table 7. It was found that writing and reading of record could be done at sufficient S/N ratio as in the case of SOAZ.

The built-up conditions of t-butyl derivative of $\text{LuH}(\text{Pc})_2$ are shown below.

Solvent: chloroform/trimethylbenzene/acetone (1/1/2)

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Concentration: 0.5 mg/ml

Aqueous phase: pure water, water temperature 20°C

Surface pressure: 20 mN/m, vertical moving speed of substrate 3 mm/min.

5 Examples 44 - 50

Recording media were prepared by use of the substrate electrode materials and the dye compounds shown in Table 8, and the same experiments as in Examples 42 and 43 were conducted with the controlled current value of the probe current set at 10^{-9} A to obtain the results shown in Table 8. As shown by the mark B in the Table, recording and reproduction could be done at sufficient resolving power and ON/OFF ratio for all of the samples.

10 The built-up number of the dye LB film was all two layers. Also, the Pt electrode was vapor deposited by use of the EB method, and ITO by the sputtering method, respectively.

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Table 7

Organic Compound	Built-up Number	a Region			b Region			Resolving Power	
		Recording Characteristic	ON/OFF Ratio	Erasability	Recording Characteristic	ON/OFF Ratio	Erasability	Not more than 0.01 μ	"
SOAZ	2	A	B	A	A	A	A	Not more than 0.1 μ	"
	4	A	B	A	A	A	A		
	8	A	A	A	A	A	A		
	1.2	A	A	A	A	A	A	Not more than 0.1 μ	"
	20	B	A	A	B	A	A		
	30	B	A	A	C	A	A		
Luh (Pc)	2	A	C	A	I	B	A	Not more than 0.03 μ	"
	4	A	B	A	A	A	A		
	8	A	B	A	A	A	A		
	12	A	A	A	A	A	A	Not more than 0.1 μ	"
	20	B	A	A	C	A	A		
	30	C	A	A	C	A	A		

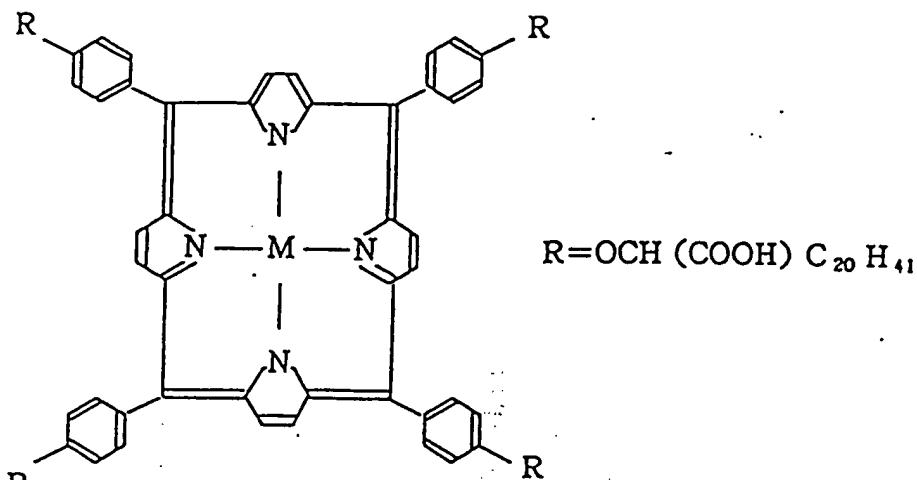
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Table 8

Example.	Substrate Electrode	Dye Compound	Recording Repro- ducibility	Resolving Power
44	Pt (100 Å)	S O A Z	O	Not more than 0.01 μ
45	Cr/Au (50 Å/400 Å)	Tetraphenylporphyrine derivative *	O	Not more than 0.05 μ
46	I TO (1000 Å)	S O A Z	O	Not more than 0.03 μ
47	Cr/Au (50 Å/400 Å)	Anthracene derivative **	O	Not more than 0.1 μ
48	Cr/Au (50 Å/400 Å)	Docosylpyradinium- tetracyanoquinodimethane	O	Not more than 0.01 μ
49	Cr/Au (50 Å/400 Å)	Pentacosa-10,12-diynoic acid	O	Not more than 0.01 μ
50	Cr/Ar (50 Å/400 Å)	Bacteriorhodopsin ***	O	Not more than 0.05 μ

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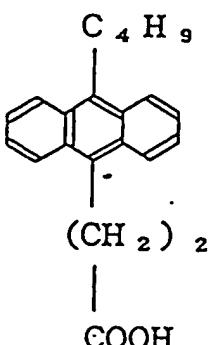
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*** violet film extracted from a cultured product obtained by culturing a highly halophilic bacterium according to the known method.

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Example 51

When the same experiments were conducted by use of the devices shown in Figs. 10D-F, in place of the devices shown in Figs. 10A-C employed in Examples 42 - 50, the same results were obtained.

In the Examples as described above, the LB method was employed for formation of the dye recording layer, but any film forming method can be used without limitation to the LB method, provided that an extremely thin film can be prepared, and specifically the vacuum vapor deposition method such as an MBE method, a CVD method, etc. may be included.

Applicable materials are not limited to only organic compounds, but organic materials such as chalcogenide compounds, etc. are also applicable.

Further, it is also possible to use an integration of the electrode and the recording layer by use of a semiconductor as the electrode on the recording medium side.

The present invention is not limitative of the substrate material, its shape and surface structure at all. More than three probes may be employed although three probes were employed in this invention.

According to the present invention, a novel recording and reproducing device having the following specific features can be provided.

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(1) Even when compared with optical recording, by far higher density recording is possible.

(2) Since the recording layer is formed by building up monomolecular films, the film thickness control could be done easily on the molecular order (several Å to several ten Å). Also, since controllability is excellent, reproducibility is high when forming a recording layer.

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be provided.

(4) The energy required for reproduction is small and the power consumption is little.

(5) The recording speed and reading speed are rapid by providing track.

(6) The error ratio is low due to track and timing signals.

5 (7) A recording resolving power of $0.01 \mu\text{m}$ or more can be obtained and a high density recording better by 2 digits or more as compared with the optical recording method of the prior art is possible.

(8) Because the energy required for reading of record is small, there is no destruction of record accompanied with reproduction. Therefore, a large capacity file memory with good stability can be realized.

10 (9) The structure of the recording medium is simple and its preparation process is also simple. Therefore, due to excellent controllability, reproducibility is high when the element is formed and also productivity is rich.

(10) The scope of organic materials and inorganic materials which can be utilized for recording medium is broad, and also a very cheap recording medium can be provided.

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Claims

20 1. A recording device, comprising a probe electrode, a recording medium exhibiting an electric memory effect and a writing voltage applying means for applying voltage on the recording medium from said probe electrode.

25 2. A reproducing device, comprising a probe electrode, a recording medium exhibiting electric memory effect, a voltage applying means which is arranged to apply a voltage not exceeding the threshold voltage giving rise to electric memory effect on the recording medium from said probe electrode and a reading means for reading the current quantity which passes through said recording medium.

30 3. A device according to claim 1 or 2, wherein said recording medium comprises a monomolecular film of an organic compound or a built-up film of said monomolecular films.

4. A device according to claim 3, wherein said organic compound has a group having π -electron level and a group having δ -electron level in the molecule.

5. A device according to claim 3, wherein said organic compound is an organic dye compound.

6. A device according to claim 3, wherein said organic compound is at least one compound selected from dyes having a porphyrine skeleton, azulene type dyes cyanine type dyes, dyes having squarilium group, dyes having croconic methine group, condensed polycyclic aromatic compounds, condensed heterocyclic compounds, diacetylene polymers, tetraquinodimethane, tetrathiafluvalene and metal complex compounds.

35 7. A device according to any preceding claim, wherein said recording medium comprises a semiconductor exhibiting electric memory effect.

8. A device according to claim 7, wherein said semiconductor is an amorphous semiconductor formed of a chalcogenide.

9. A device according to claim 8, wherein said chalcogenide contains at least one element of the groups III, IV, V and VI of the periodic table and at least one element of Se, Te and As.

10. A device according to claim 7, wherein said semiconductor is a silicon film.

11. A device according to claim 10, wherein said silicon film is an amorphous silicon film.

12. A device according to claim 11, wherein said amorphous silicon is a p^+ /n/i laminate or n^+ /p/i laminate.

13. A device according to claim 7, wherein semiconductor is an organic semiconductor.

14. A device according to claim 13, wherein said organic semiconductor is a compound containing an electron acceptor and a metal.

15. A device according to claim 14, wherein said electron acceptor is tetracyanoquinodimethane, tetracyanoethylene, or tetrafluorotetracyanoquinodimethane, tetracyanonaphthoquinodimethane.

16. A device according to any preceding claim, wherein a plural number of said probe electrodes are provided.

17. A reproducing device, comprising a probe electrode, a recording medium written by an energy beam irradiation, a means for applying a voltage onto said recording medium from said probe electrode and a means for reading the change in the current quantity flowing through said recording medium.

18. A reproducing device according to claim 17, wherein said recording medium is formed of a semiconductive substance having a conductivity of $10^{-10} (\text{ohm.cm})^{-1}$ or higher.

19. A reproducing device according to claim 18, wherein said recording medium is formed of a semiconductive substance having a conductivity of $10^{-8} (\text{ohm.cm})^{-1}$ or higher.

20. A reproducing device according to claim 18 or 19, wherein said semiconductive substance is a semiconductive substance containing at least one selected from the group of elements consisting of elements of the group IVB, elements of the group III, elements of the group VB, elements of the group IIB and elements of the group VIB of the long period type periodic table.

21. A reproducing device according to claim 20, wherein said semiconductive substance is a

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semiconductive substance containing at least one selected from the group of substances consisting of Si, Ge, Ga, As, GaP, InAs, InP, CdS, CdSe, ZnO and ZnS.

22. A reproducing device according to any of claims 17 to 21, wherein said recording medium comprises a monomolecular film of an organic compound or a built-up film of said monomolecular films.

23. A reproducing device according to claim 22, wherein said organic compound has a group having π -electron level in the molecule. 5

24. A reproducing device according to claim 22, wherein said organic compound is at least one compound selected from the group consisting of aromatic polycyclic compounds, polymeric compounds having conjugated π bond, photochromic compounds, polypeptide compounds, a compound in a dye association state, and electron transfer complexes. 10

25. A generating device according to any of claims 17 to 24, wherein said energy ray is an electron beam, an ion beam, a laser beam, an X-ray, an UV-ray or visible light.

26. A device according to any preceding claim, wherein said recording medium is disposed between said probe electrode and a counter-electrode disposed in opposition to said probe electrode.

27. A device according to claim 3 or 22, wherein said monomolecular film or built-up film has a film thickness in the range of several Å to several 1000 Å. 15

28. A device according to claim 27, wherein said monomolecular film or built-up film has a film thickness in the range of several Å to 500Å.

29. A device according to claim 28, wherein said monomolecular film or built-up film has a film thickness in the range of 10 Å to 200 Å. 20

30. A device according to claim 27, 28 or 29, wherein said monomolecular film or built-up film is a film formed by an LB method.

31. A device according to any preceding claim, having a XY scanning driving means for said probe electrode.

32. A device according to any of claims 1 to 30, comprising a means for fine controlling three-dimensionally the relative positions of said probe electrode and recording medium. 25

33. A reproducing device according to claim 2 or 17, wherein said reading means has a servo circuit.

34. A reproducing device according to claim 2 or 17, wherein said reading means comprises an A/D transducer.

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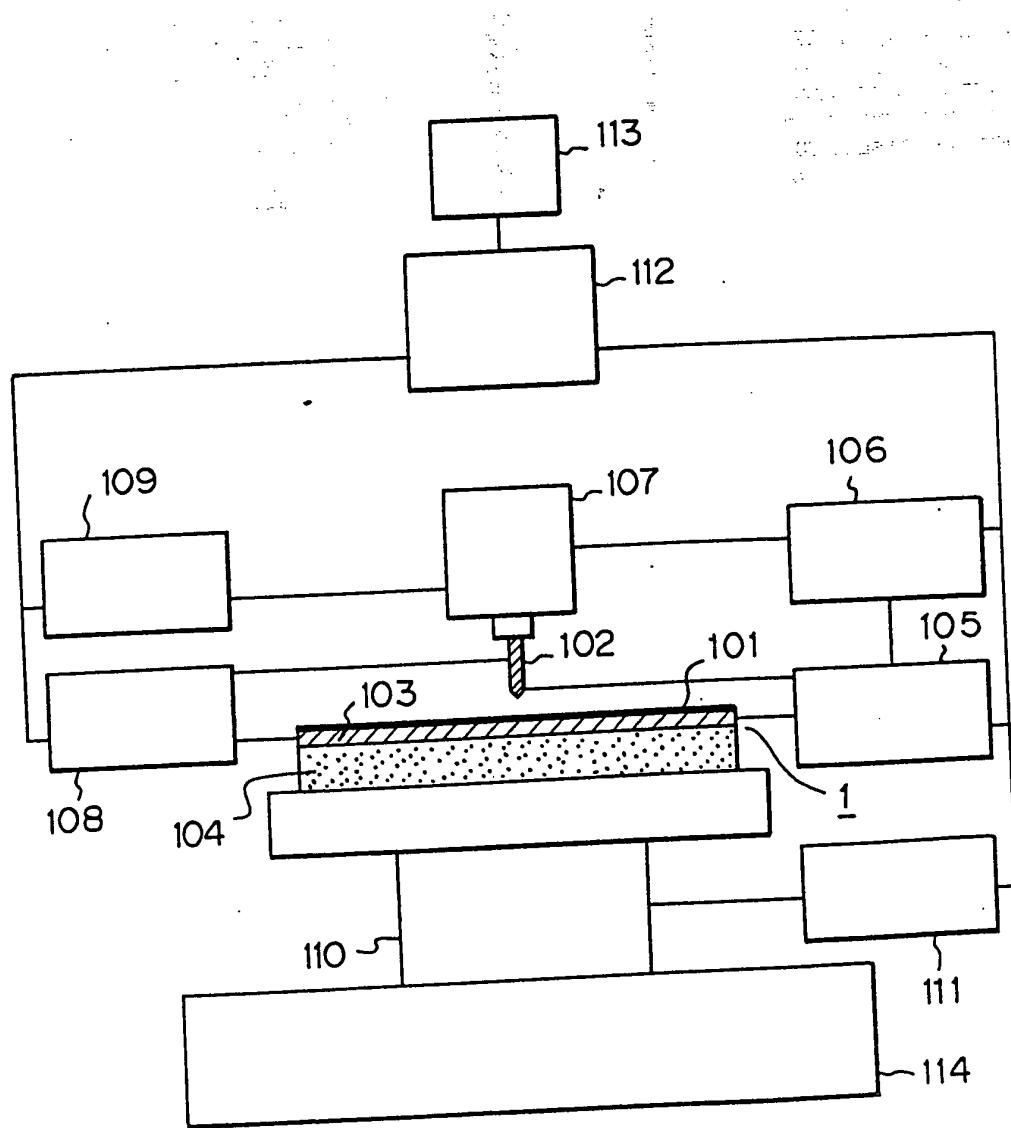
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Fig. 1



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Fig. 2

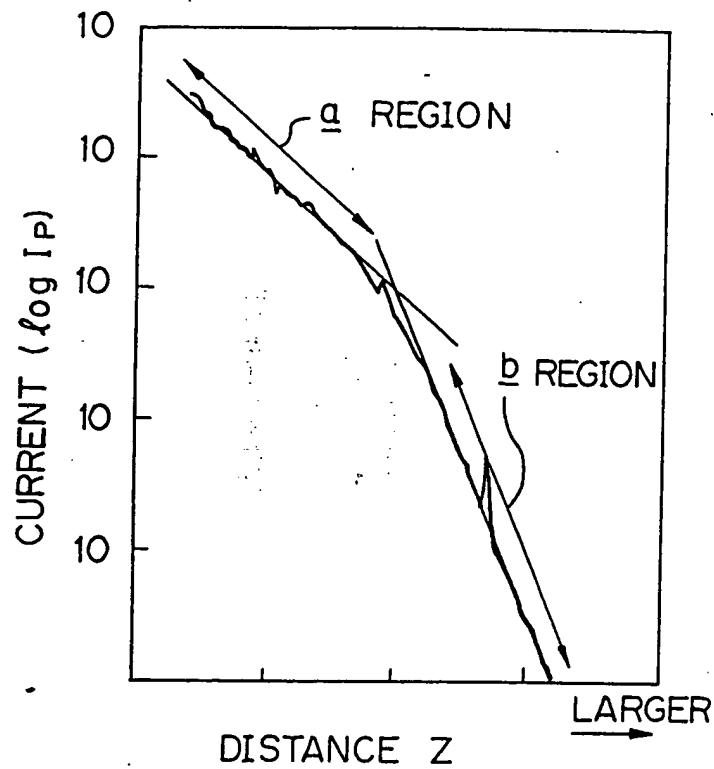
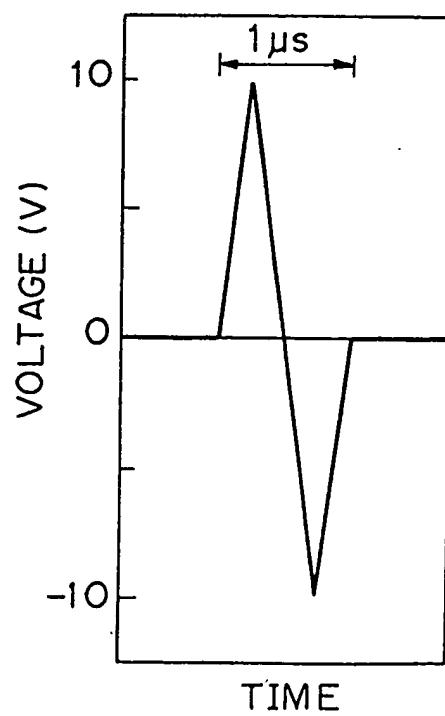


Fig. 3



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Fig. 4

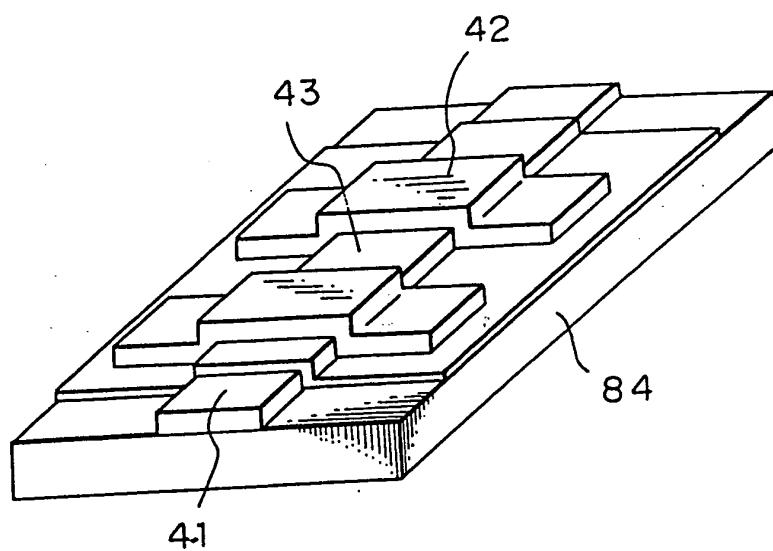
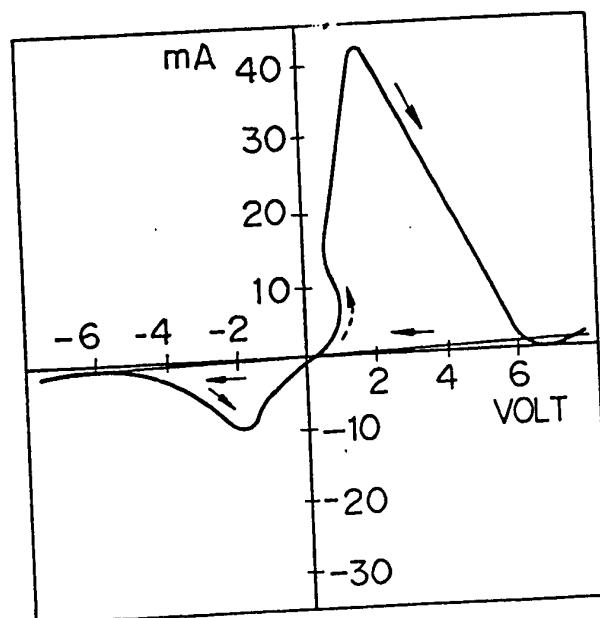
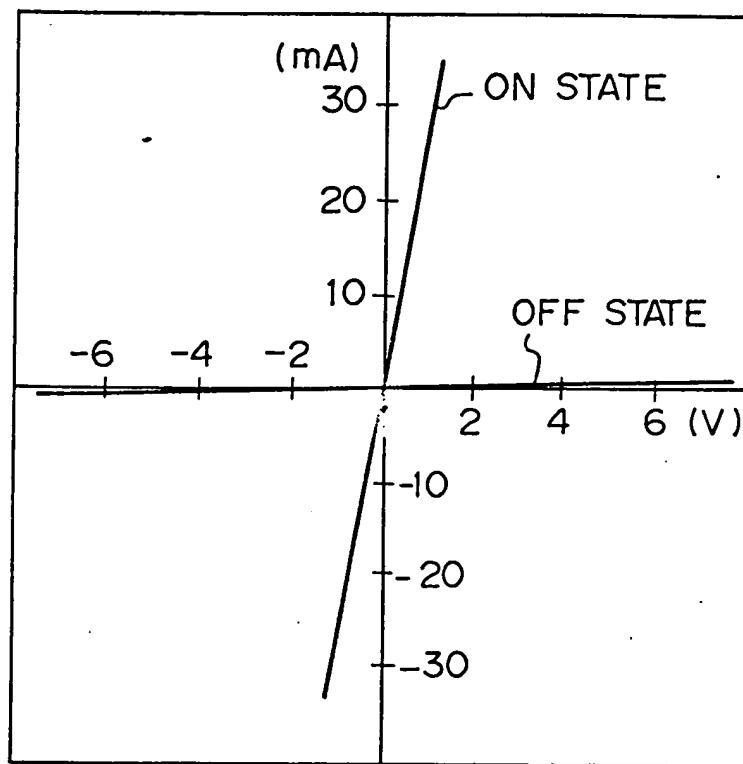


Fig. 5



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Fig. 6



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Fig. 7

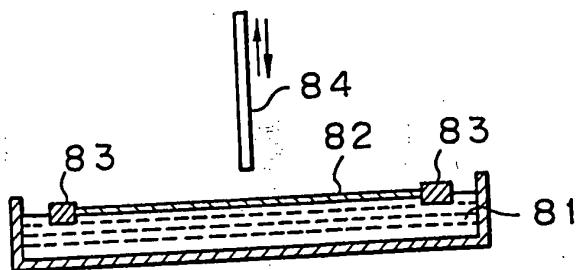


Fig. 8 A

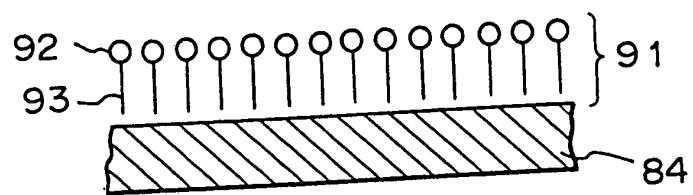
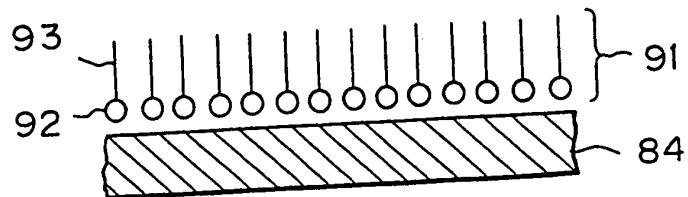


Fig. 8 B



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Fig. 9A

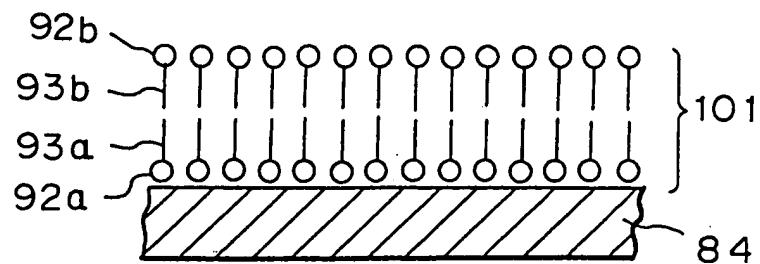


Fig. 9B

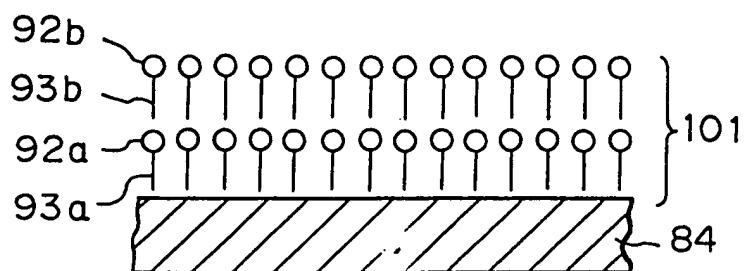
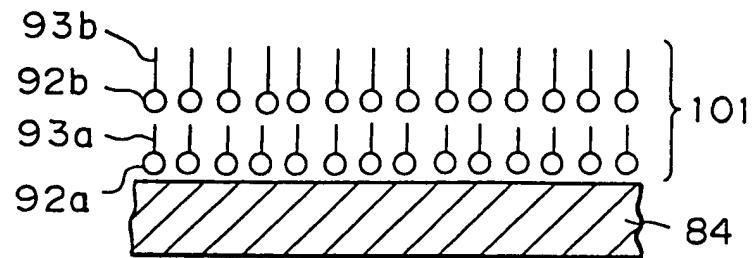
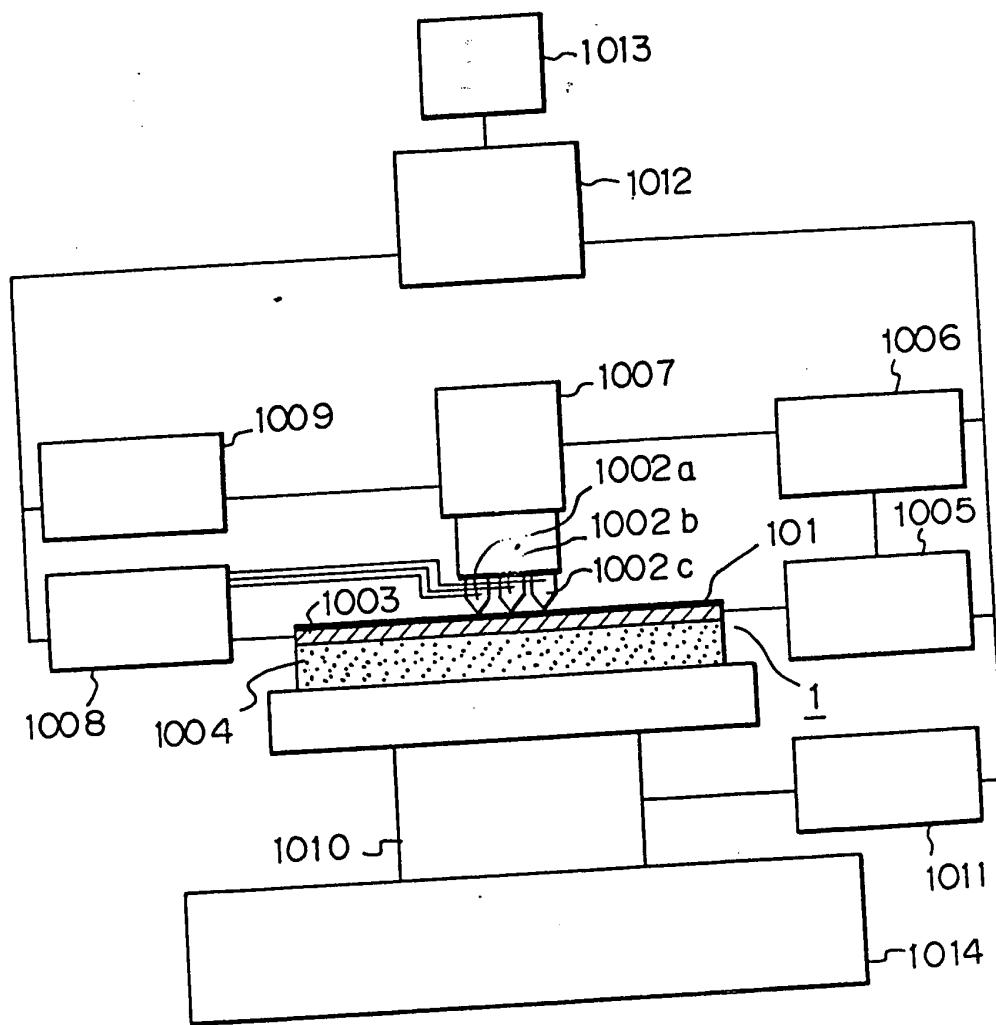


Fig. 9C



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Fig. 10A



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Fig. 10B

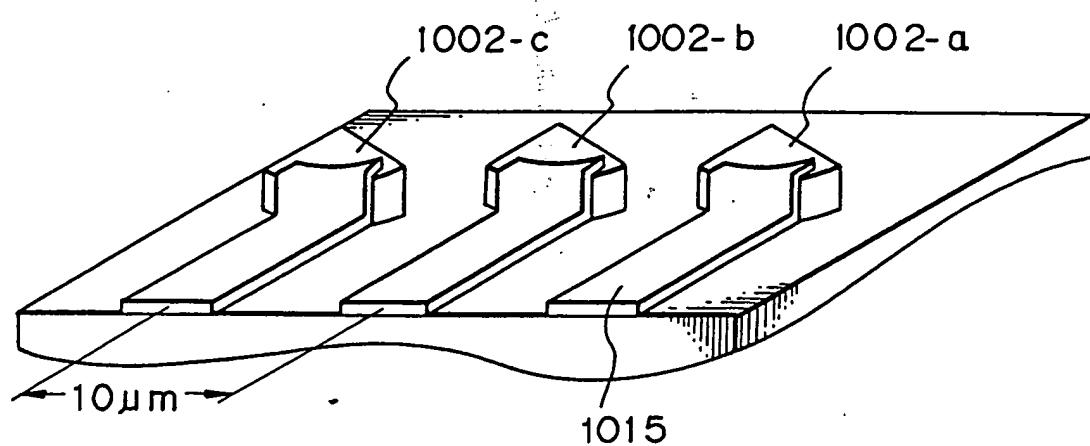
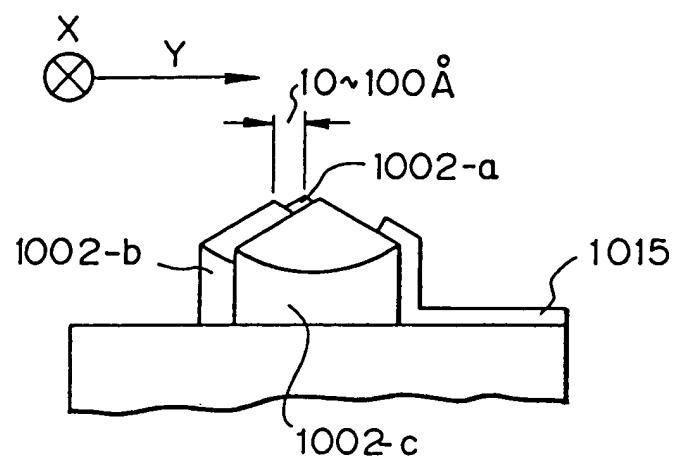
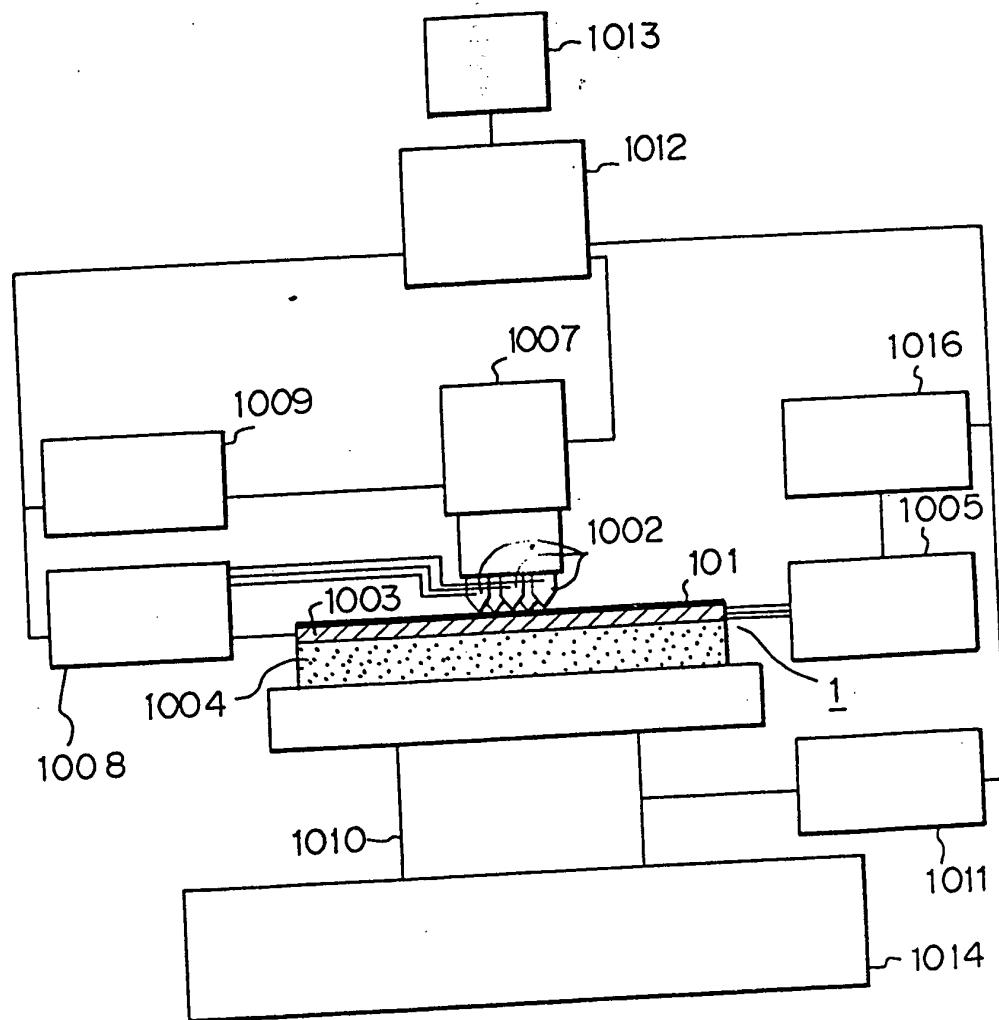


Fig. 10C



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Fig. 10 D



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Fig. 10E

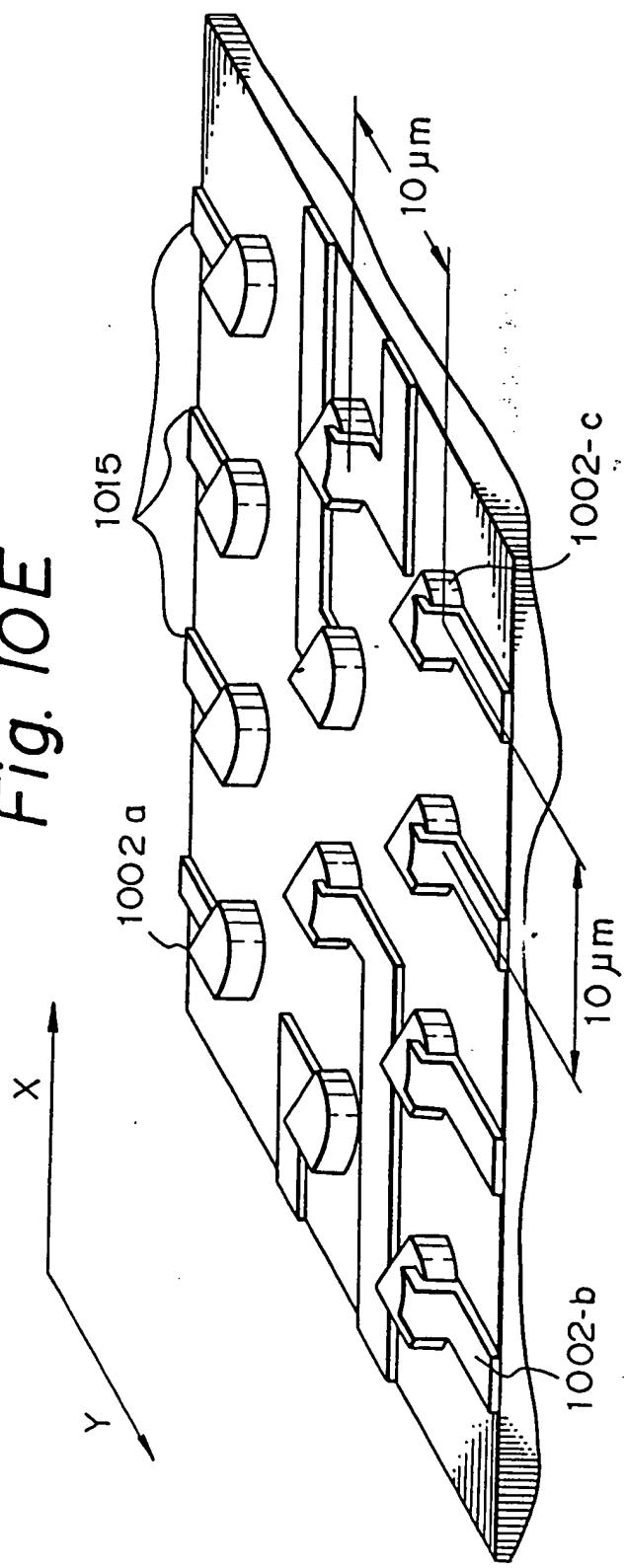
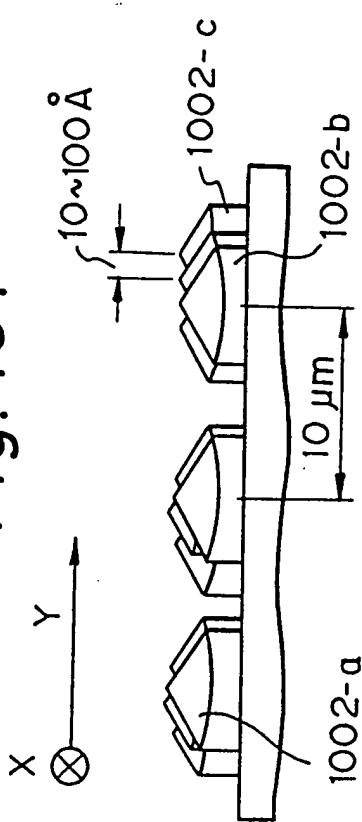
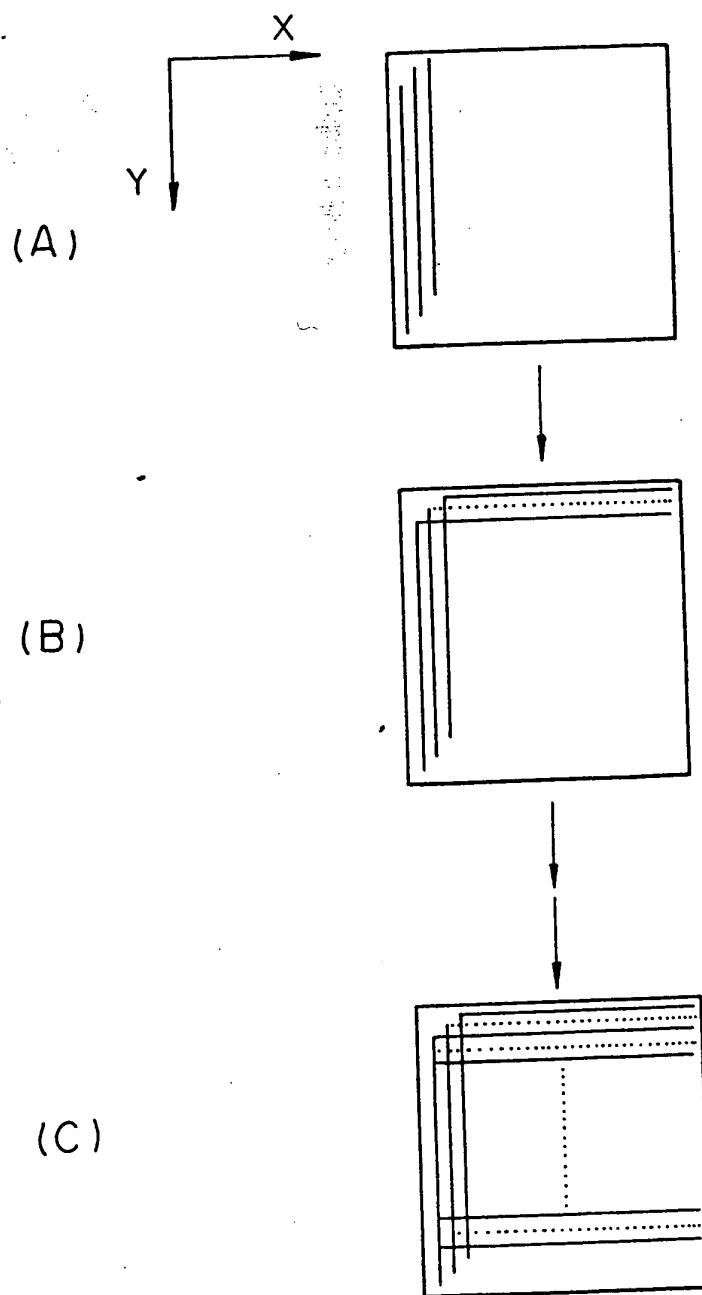


Fig. 10F



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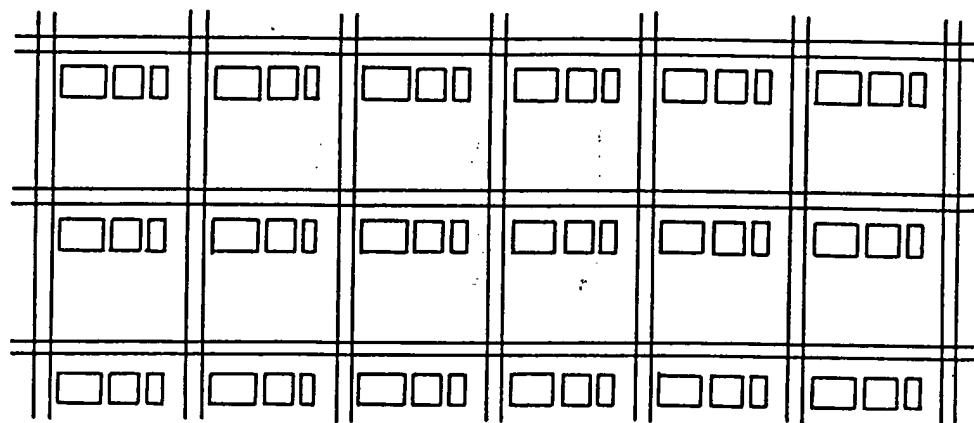
Fig. 11



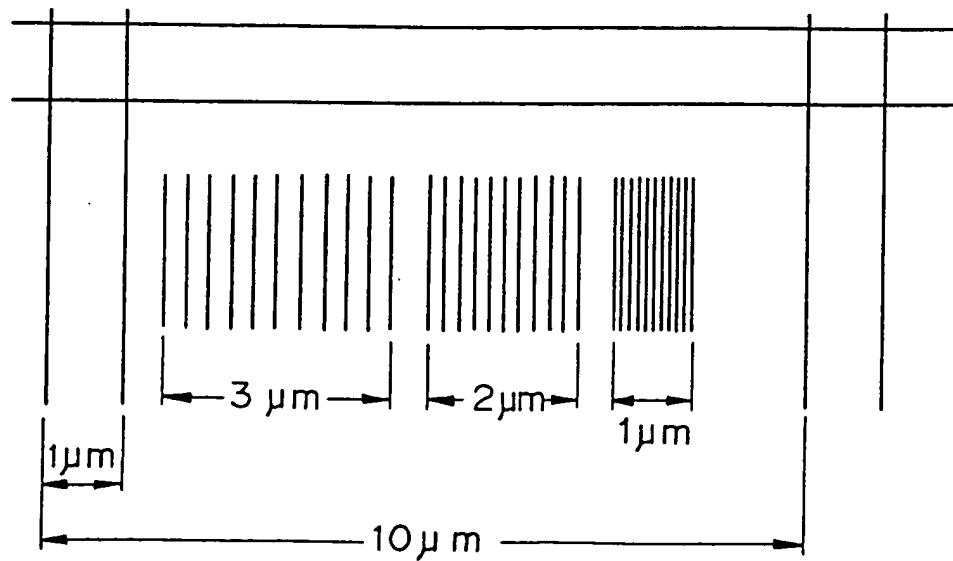
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Fig. 12

(a)



(b)



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